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Engineering Assessment of EDB (Ethylene Dibromide) Pesticide Pesticide Destruction Technologies

PEI Associates, Inc., Cincinnati, OH

Prepared for

Environmental Protection Agency, Cincinnati, OH

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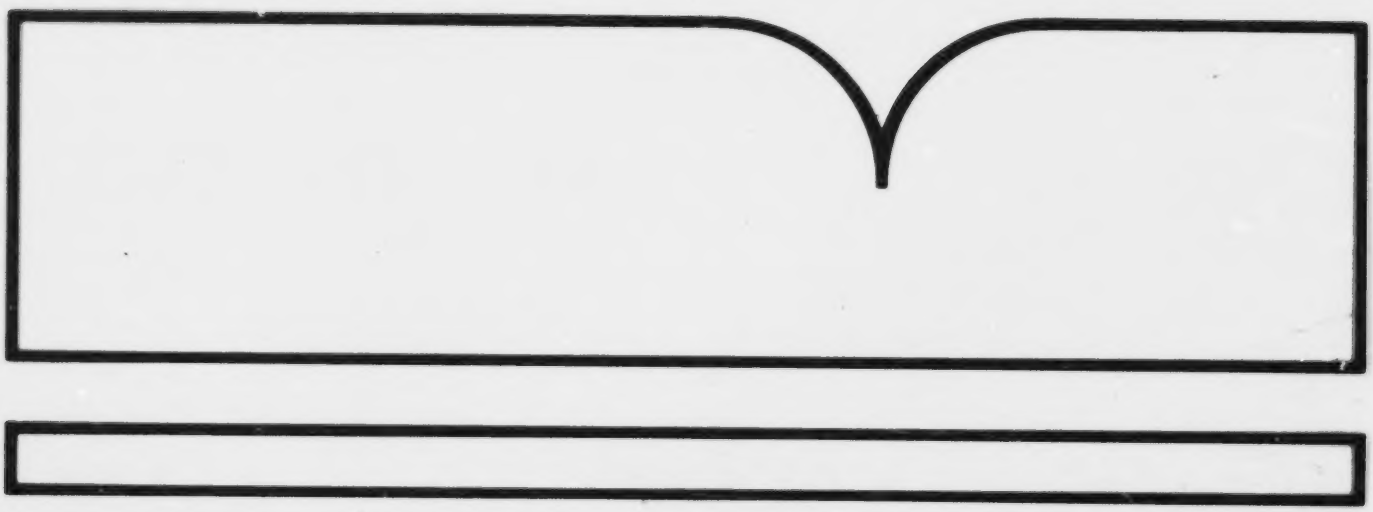

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16. ABSTRACT

The project covered by this report involved an engineering evaluation of the suitability of various available technologies for the destruction of ethylene dibromide pesticides. The purpose of the study was to highlight the technical merits and shortcomings, safety, cost, and total time requirement for each of the alternatives considered.

Both thermal and chemical destruction options were considered. Evaluation criteria were developed so that the different options could be compared on a common basis. Information was collected on each candidate process through a literature search and discussions with industry experts. Concurrent with these efforts, bench-scale tests of the chemical methods were conducted. Also, a test burn was made at a commercial facility to determine the effectiveness of one of the incineration options. The results of these tests were factored into this report. Because the chemical processes are still in the conceptual stages, only preliminary process calculations and cost estimates were developed for these processes.

Based on the results of this study, incineration in the presence of sulfur dioxide appears to be the best alternative for the safe, effective, rapid, and economical destruction of the ethylene dibromide pesticides.

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ENGINEERING ASSESSMENT OF EDB PESTICIDE DESTRUCTION TECHNOLOGIES

by

Sunil H. Ambekar and Bernard A. Laseke
PEI Associates, Inc.
11499 Chester Road
Cincinnati, Ohio 45246

EPA Contract No. 68-03-3389

Project Officer Edward R. Bates
Risk Reduction Engineering Laboratory (RREL)
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

RISK REDUCTION ENGINEERING LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OH 45268

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of materials that, if improperly dealt with, can threaten both public health and the environment. The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water systems. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Risk Reduction Engineering Laboratory is responsible for planning, implementation, and management of research, development, and demonstration programs to provide an authoritative, defensible engineering basis in support of the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

The project covered by this report involved an engineering evaluation of the suitability of various available technologies for the destruction of ethylene dibromide pesticides. The purpose of the study was to highlight the technical merits and shortcomings, safety, cost, and total time requirement for each of the alternatives considered.

E. Timothy Oppelt, Acting Director
Risk Reduction Engineering Laboratory

ABSTRACT

Under the authority of the Federal Insecticide, Fungicide, and Rodenticide Act, the U.S. Environmental Protection Agency (EPA) suspended and cancelled the registrations and prohibited the further use, sale, and distribution of ethylene dibromide (EDB) pesticide formulations. As a part of this ban, EPA also assumed the responsibility for destroying/disposing of existing EDB stocks.

The project covered by this report involved an engineering evaluation of the suitability of various available technologies for the destruction of ethylene dibromide pesticides. The purpose of the study was to highlight the technical merits and shortcomings, safety, cost, and total time requirement for each of the alternatives considered.

Both thermal and chemical destruction options were considered. Evaluation criteria were developed so that the different options could be compared on a common basis. Information was collected on each candidate process through a literature search and discussions with industry experts. Concurrent with these efforts, bench-scale tests of the chemical methods were conducted. Also, a test burn was made at a commercial facility to determine the effectiveness of one of the incineration options. The results of these tests were factored into this report. Because the chemical processes are still in the conceptual stages, only preliminary process calculations and cost estimates were developed for these processes.

Based on the results of this study, incineration in the presence of sulfur dioxide appears to be the best alternative for the safe, effective, rapid, and economical destruction of the ethylene dibromide pesticides.

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ABBREVIATIONS AND ACRONYMS

ATEG	Sodium Hydroxide Tetraethylene Glycol Process
DRE	Destruction Removal Efficiency
EDB	Ethylene dibromide
EDC	Ethylene dichloride
EPA	Environmental Protection Agency
FIFRA	Federal Insecticide, Fungicide, and Rodenticide Act
FRP	Fiberglass reinforced plaster
IDLH	Immediately Dangerous to Life or Health
KTEG	Potassium Hydroxide Tetraethylene Glycol Process
PIC	Products of Incomplete Combustion
POHC	Partially Oxidized Hydrocarbons
RCRA	Resource Conservation and Recovery Act
RTI	Research Triangle Institute
SCW	Super Critical Water
TEG	Tetraethylene Glycol
TLV	Threshold Limit Value

CONVERSION FACTORS

1 foot = 0.3048 meter

1 pound = 454.55 grams

1 cubic foot = 7.481 U.S. gallons

1 cubic foot = 0.02832 cubic meter

1 gm/cc = 62.43 lb/ft^3

1 gm/cc = 8.345 lb/gallon (U.S.)

760 mm of Hg = 1 atmosphere

760 mm of Hg = 14.7 psi

$$°C = \left(\frac{°F-32}{9}\right) \times 5$$

$$°K = °C + 273.15$$

$$°R = °F + 459.7$$

1 kilowatt = 1.341 h.p.

1 calorie = 3.97×10^{-3} Btu

Gas constant $R = 82.06\ (cm^3)(atm)/(g.mole)(°K)$

$R = 10.73\ (lb/in^2)(ft^3)/(lb.mole)(°K)$

SECTION 1

INTRODUCTION

BACKGROUND

In September 1983 and February 1984, the U.S. Environmental Protection Agency (EPA) suspended the registrations and later finally prohibited (i.e., "cancelled") the further use, sale, and distribution of ethylene dibromide (EDB) pesticide formulations. This action was taken under the authority of the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) as a result of animal studies on health effects, evidence of EDB-contaminated water, evidence of EDB-contaminated food, and EPA-sponsored risk-benefit analyses. As part of this regulatory action, EPA issued orders which halted the use of EDB-containing material and requested manufacturers and distributors to recall all existing EDB products. EPA was also required to indemnify all registrants and other owners of EDB pesticides for their economic losses, and to take responsibility for the destruction/disposal of the EDB stocks (McCarthy et al., 1987).

The total quantity of formulated EDB pesticides identified for Agency disposal amounts to approximately 346,000 gallons or 3.7 million pounds. Of this amount, 1.1 million pounds are EDB. For purposes of background information, the various EDB formulations are divided into four categories. These categories and their associated approximate quantities are shown below:

Category	Quantity, 10^3 gallons
1. CS_2-containing formulations	132
2. Chloropicrin-containing formulations	70
3. Methyl bromide-containing formulations	19
4. Miscellaneous formulations	125

PURPOSE

This study was prepared for the EPA Risk Reduction Engineering Laboratory (RREL) to provide an engineering evaluation of the candidate EDB destruction technologies.

TECHNICAL APPROACH

The technical approach adopted for this study differentiates it from previous studies of EDB disposal alternatives in that it concerns engineering alternatives as opposed to management alternatives. The focus of the effort of this study was directed to the following progression of steps:

1. The engineering evaluation project was viewed as the first step in a larger EDB destruction program that could either proceed through a multiple parallel pilot plant test program and then continue at the production scale through detailed design and engineering, facility fabrication and construction, startup and shakedown, and operation and decommissioning of a new facility, or proceed through a test destruction program at an existing facility, followed by destruction of all stocks.

2. The engineering evaluation involved the identification of candidate technologies and processes, the development of selection criteria, and the application of selection criteria to support technical judgments.

3. Vendor contacts were made to the various incineration facility operators to determine interest, feasibility, and cost to destroy the EDB formulations.

4. Preliminary process designs and cost estimates were developed for the selected chemical destruction processes in order to compare these processes to the incineration processes on an equal basis.

5. Process design and cost packages were developed by working closely with the EPA process developers. Bench-scale performance data were used to support equipment design and operating assumptions.

6. The results of a parallel bench-scale laboratory study were factored into the analysis to support and expand the EPA bench-scale work.

7. A trial burn of two EDB formulations was separately contracted for by the EPA to obtain more information on incineration in the presence of sulfur dioxide (SO_2) to facilitate bromine scrubbing. Data from this test were then factored into the evaluation of all alternatives.

SCOPE OF WORK

The scope of work performed to complete the technical approach described above involved the following tasks:

1. PEI identified all candidate technologies and processes that were available to destroy the EDB pesticide stocks. The scope of technology search covered all technologies and processes that were commercial or developmental with the promise of near term availability.

2. PEI developed selection criteria to evaluate the candidate technologies. The criteria considered such parameters as maturity, access, feasibility, operability, auxiliary processing needs, health and safety, secondary environmental impact, and permitting.

3. The candidate technologies were evaluated against the selection criteria through a two-step screening and detailed evaluation procedure. A number of technologies and processes were selected for detailed evaluation. As part of the detailed evaluation process, fundamental physical and chemical data were collected, process design developments were researched, preliminary process designs were developed, vendor quotations were obtained and process costs were estimated, and performance capabilities were assessed.

ORGANIZATION OF REPORT

The report is organized in a manner consistent with the overall purpose of the project. In Section 2, the methodology used to complete the study is described. In this section, we introduce the evaluation criteria and describe the costing procedures. In Section 3, we classify the technologies, describe the technologies and processes investigated, and focus on those selected for detailed evaluation. In Section 4, we present the results of the study. The results are presented and described in terms of the evaluation criteria presented in Section 2. In Section 5, conclusions and recommendations are presented. Three appendices provide documentation and backup information for process calculations, cost calculations, and vendor contacts.

SECTION 2

METHODOLOGY

EVALUATION CRITERIA

As mentioned earlier, the purpose of this study was to provide an engineering evaluation of the candidate EDB destruction technologies. The aim of the evaluation was to highlight the technical merits and shortcomings, safety, cost, and total time requirement for each of the alternatives considered. To provide a common basis to compare different process options, the following evaluation criteria were developed in consultation with EPA:

CRITERIA

- Status - Commercial, Pilot-Scale, or Conceptual
- Accessibility
- Past Experience
- Need for Development and Testing
- Preprocessing
- Process Safety
- Toxic Emissions
- Residues
- Need for New/Additional Equipment
- Extent of Corrosion
- Process Compatibility with Pesticides
- Secondary Environmental Impact and Health Considerations
- Mechanical Reliability
- Transportational Access to Facility
- Storage and Handling of Pesticides and Residues
- Cost
- Permitting
- Probability of Success
- Time for Completion

All the items in the above criteria are self explanatory. An attempt was made to make the criteria exhaustive and to cover all major technical and

economic aspects. Information was collected on each candidate process so as to address each item in the evaluation criteria. This was done by an exhaustive literature survey, discussions with industry experts, process calculations, and preliminary cost estimates. The results are presented in Section 4.

COST ESTIMATING PROCEDURE

Process economics is an important factor in the ultimate selection of a technology. To compare the cost-effectiveness of each option, unitized costs ($/lb of pesticide) were established for each process option. Unitized costs for technologies which are already commercialized (incineration and cement kiln incineration) were obtained by contacting vendors and getting their best possible estimates. As regards chemical destruction, both the process options available therein are still in the conceptual stages. On the basis of laboratory scale results, preliminary flow sheets were developed (Section 3) followed by preliminary process design (Appendix A) and preliminary cost estimates (Appendix B). Details on the cost estimating procedure adopted are presented in Appendix B. The various assumptions underlying the design have been stated in Appendix A.

SECTION 3

DESCRIPTION OF TECHNOLOGIES

A wide range of existing technologies may have a potential for successfully eliminating ethylene dibromide (EDB) pesticide formulations. Research Triangle Institute (RTI) performed a preliminary screening of available technologies for the EPA (RTI, 1987). The technologies were evaluated against the following criteria:

1) Immediate availability of the technology and the potential of procurement of a permit within the next 2 years.
2) Capability of meeting the letter and intent of the RCRA and FIFRA regulations.
3) Capability of handling the corrosivity and emissions due to EDB.

The following technologies were selected in this engineering evaluation as possible candidates for the elimination of EDB pesticide formulations:

1) Incineration in a waste incinerator under oxidizing (excess air) conditions (conventional incineration)
2) Starved-air incineration
3) Incineration in presence of sulfur dioxide or sulfur-containing waste
4) Incineration in a cement kiln
5) Chemical destruction by the ATEG process
6) Chemical destruction using the zinc process
7) Williamson's synthesis for the destruction of methyl bromide
8) MODAR process (oxidation in supercritical water)

CLASSIFICATION OF PROCESSES

The preceding technologies can be classified into two main categories: 1) thermal destruction, and 2) chemical destruction.

Thermal Destruction

Conventional incineration, incineration in the presence of sulfur dioxide, starved-air incineration, and cement kiln incineration fall into

this category. Thermal destruction uses heat to convert hazardous materials into harmless or less toxic materials. Depending on the conditions prevailing in an incinerator, the thermal destruction processes can be further classified into three subclasses:

1) Conventional incineration or excess air oxidation--thermal decomposition in the presence of excess air (oxygen).
2) Pyrolysis--thermal decomposition in the absence of oxygen.
3) Starved-air incineration--incineration that uses substoichiometric amounts of air.

All of the options currently under consideration (except starved air incineration) would be classified as conventional incineration. Cement kiln incineration can be regarded as a special application of conventional incineration because of the oxidizing conditions in the kiln.

Chemical Destruction

In chemical destruction, the waste is reacted with a suitable reagent to yield products that are harmless or less toxic than the parent compounds. The ATEG process, the zinc process, and Williamson's synthesis fall into this category. The MODAR process is also classified as a chemical process, although, like incineration, it oxidizes the wastes to less harmful products. Supercritical water, however, is used as an oxidizing medium in the MODAR process.

PROCESSES SELECTED FOR DETAILED EVALUATION

Based on the selection criteria developed earlier in Section 2, certain processes were selected from the earlier evaluation for more critical review. The processes considered in the final evaluation are as follows:

1) Conventional incineration
2) Conventional incineration in the presence of sulfur dioxide
3) Starved-air incineration
4) Cement kiln
5) ATEG process
6) Zinc process

A brief description of each of these processes is presented in the following subsections.

Conventional Incineration (Excess-Air Incineration)

Conventional incineration is the most common way of destroying hazardous substances. Numerous commercial hazardous waste incinerators are operating successfully throughout the United States and worldwide. Some of these operating systems are transportable, which makes them convenient for the destruction of hazardous wastes at specific sites.

This process uses combustion to oxidize hazardous materials to harmless or less toxic materials. Products of incineration consist of combustion gases and, in some cases, solid residues. Most liquid wastes like the EDB formulations yield gaseous products. Although incineration may assure complete destruction of the hazardous waste, the combustion products can be environmentally harmful and, thus, require secondary treatment. This secondary treatment may be wet scrubbing, particulate collection, or the use of afterburners. The technology cannot be used to destroy wastes whose combustion products cannot be treated to abate harmful emissions. Wastes containing compounds of sulfur, phosphorus, nitrogen, and chlorine have been successfully treated by this technology; however, no routine incineration runs of brominated wastes are known.

Figure 3-1 presents a typical flowsheet of a hazardous waste incineration system. The plant can be divided into three main areas: 1) the storage, handling, and preparation of the waste fuel prior to incineration; 2) the incinerator itself; and 3) the emissions control system.

The storage and handling area is concerned with the receiving and storage of the waste at the site. Some waste must be preprocessed before incineration to achieve the necessary heating value or to reduce the viscosities

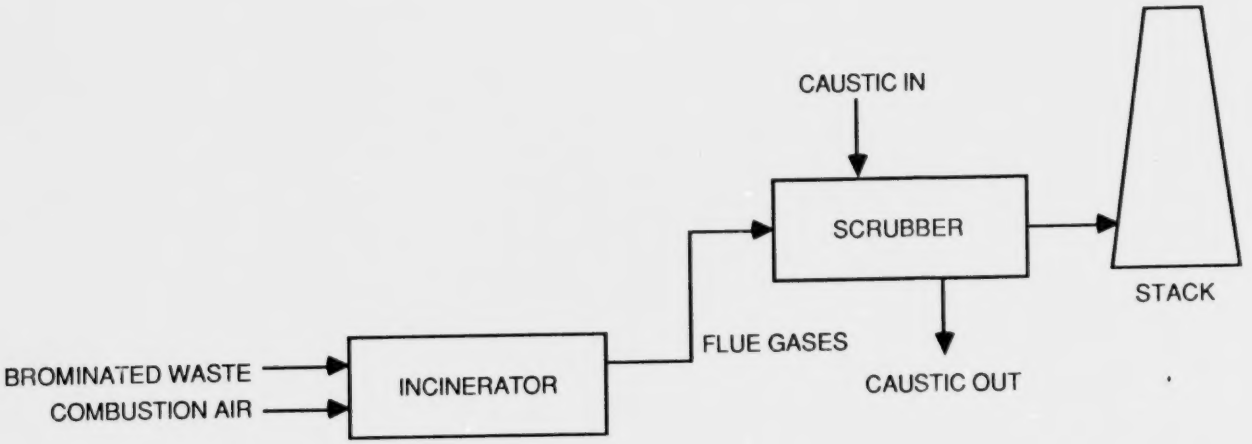


Figure 3-1. Schematic flow diagram of conventional incineration system.

to a point where the material is pumpable and atomizable at the operating temperatures. This is usually done by blending the waste with other wastes or with an auxiliary fuel in the preprocessing area. This area must be well designed to prevent or contain any spillage and resulting emissions. Bonner et al. (1981) present an excellent overview of the various available design options. This area is believed to be well designed in most operating facilities.

The preprocessed fuel is fed into the incinerator, which can be a rotary kiln, a fluidized-bed combustor, liquid injection incinerator or an electric furnace. The choice of incinerator depends on the type of waste to be destroyed. Rotary kiln, liquid injection, and fluidized-bed designs are better suited for incineration of liquid wastes than are the other two designs (Bonner et al., 1981). Most commercial incineration facilities have a rotary kiln incinerator. Typical temperatures in the combustion chamber range from 1800° to 2400°F, and under these conditions, the waste mixture undergoes instant oxidation. Liquid injection incinerators are operated under similar temperature range, although they can be operated at higher temperatures.

Because of the high operating temperatures, the furnace has to be refractory-lined. The quality of the refractory lining depends on the corrosivity of the gases likely to be generated in the incinerator. For applications involving halogenated wastes, the refractory lining must be corrosion-resistant. Typical residence times in the incinerator vary from 0.5 to 2 seconds at a minimum.

The combustion gases from the incinerator are further processed in the gas treatment area to minimize toxic emissions. For all hazardous waste

applications, this area includes a well-designed scrubbing system and, sometimes, an afterburner. If the combustion products of the primary combustor are expected to contain partially oxidized compounds, an afterburner is required to ensure complete combustion of all constituents. This eliminates the possibility of emitting partially oxidized products into the atmosphere. Some partially oxidized organics are carcinogenic and may be even more harmful than the parent compounds. If the flue gases are expected to have high concentrations of sulfur dioxide, nitrogen dioxide, hydrochloric acid, and other toxic products, a high-efficiency scrubbing system is needed to neutralize these pollutants. Venturi scrubbers are quite common for scrubbing applications, and their capabilities for particulate removal are excellent. When lime slurry is used as the scrubbing medium, toxic pollutants such as sulfur dioxide and hydrogen chloride can also be removed efficiently as long as they are not present in high concentrations. For halogenated wastes, scrubbers that have good mass transfer characteristics are recommended. Typically, a packed tower or a plate column can be used because they have excellent mass transfer characteristics and are easy to operate. If particulate emissions are the only concern, fabric filters or electrostatic precipitators (ESPs) provide adequate treatment of the flue gases. Details on the various design and operational aspects of an incinerator are presented by Bonner et al. (1981) and Sittig (1979).

Unlike fluorine and chlorine, which generate predominantly hydrogen halides upon combustion in excess air, brominated wastes generate bromine when incinerated, which is difficult to remove from the flue gases by currently operational gas-processing techniques. Caustic is typically used as the

scrubbing medium in many hazardous waste incinerators; however, it is believed that a caustic solution may not remove bromine as readily as it does hydrogen bromide. Therefore, modification of the incinerator operating conditions (e.g., addition of sulfur) will be required to prevent significant amounts of bromine emission into the atmosphere. Alternatively, if a scrubbing medium could be found which reacts rapidly with bromine, conventional incineration without any process modifications could become a viable option. The literature suggests some mediums for this application. However, more research will be required before a full-scale operation can be undertaken.

Incineration in Presence of Sulfur Dioxide or Sulfur-Containing Waste

A process modification of the conventional incineration reduces toxic emissions due to halogenated wastes. Under this option, the halogenated waste is burned in a conventional incinerator in the presence of sulfur dioxide or sulfur-containing wastes. Under the incinerator operating conditions, sulfur dioxide reacts with the halogen produced during incineration to form hydrogen bromide and sulfuric acid. During the Rollins test burn on EDB stock, 10 percent sulfuric acid (H_2SO_4) was used as the source of sulfur (Alliance Corporation, 1988). Under the kiln conditions, the H_2SO_4 decomposes as follows (Equations 1 and 2):

$$2\ H_2SO_4 \xrightarrow{\Delta} 2\ SO_3 + 2\ H_2O \qquad (1)$$

$$2\ SO_3 \underset{}{\overset{\Delta}{\rightleftharpoons}} 2\ SO_2 + O_2 \qquad (2)$$

At high temperatures, the equilibrium reaction is displaced to the right, thus favoring decomposition. The bromine formed due to oxidation of EDB (Equation 3) reacts with SO_2 and water to form hydrogen bromide (HBr) and H_2SO_4 (Equation 4).

$$C_2H_4Br_2 + 3O_2 \xrightarrow{\Delta} 2CO_2 + 2H_2O + Br_2 \qquad (3)$$

$$Br_2 + SO_2 + 2\,H_2O \longrightarrow 2\,HBr + H_2SO_4 \qquad (4)$$

The above reaction proceeds in both the gas and liquid phases.

Since the resulting acids can be easily removed in the downstream processing units (scrubbers), the problem of halogen emissions is completely eliminated (Fabian et al., 1979). A flow diagram of this process is shown in Figure 3-2. Sulfur dioxide or sulfur-containing waste in slight excess of the stoichiometric requirements should be supplied to ensure total conversion of the halogens to hydrogen halides.

Starved-Air Incineration

This option uses the same equipment and entails the same process flow as the conventional incineration process. The only difference is in the process conditions in the incinerator. Unlike conventional incineration, starved-air incineration uses less than stoichiometric quantities of air for combustion purposes. To date, the application of this technology for hazardous wastes has been minimal (Bonner et al., 1981). Some of the advantages of this process include high thermal efficiencies, reduced volume of flue gases, and suppression of particulate emissions.

The bromine/hydrogen bromide chemical equilibrium favors hydrogen bromide formation under reducing conditions (less oxygen) in the furnace. Because hydrogen bromide is more easily scrubbed than bromine is, the possibility of toxic emissions due to bromine is lessened. Thus, conceptually, starved-air incineration appears to have the potential to destroy brominated wastes.

Figure 3-3 (J. Cegielski, John Zink Co., personal communication) presents a proposed flowsheet for the application of this technology. The waste

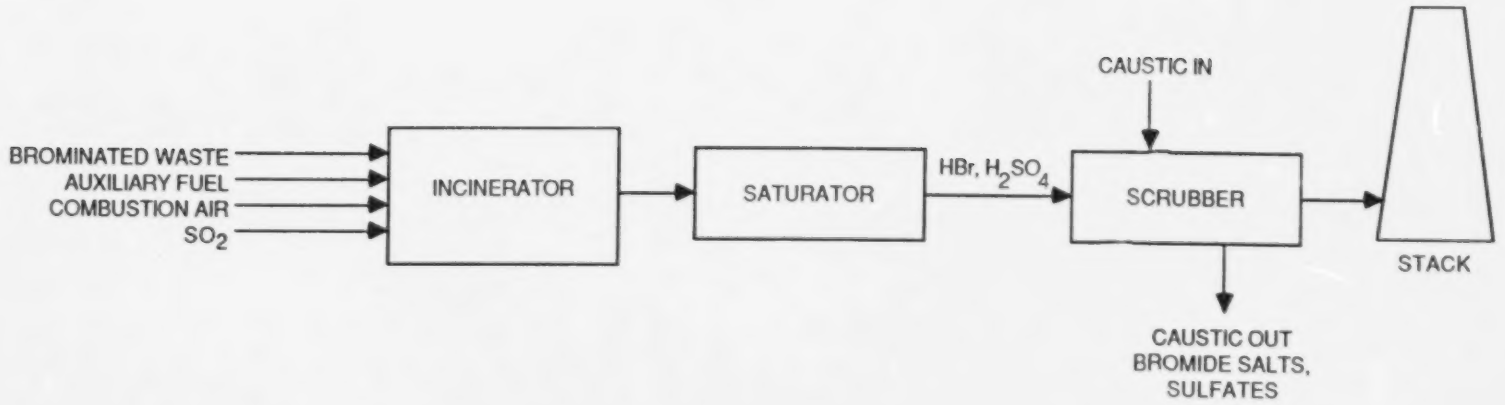


Figure 3-2. Schematic flow diagram for incineration in presence of SO_2.

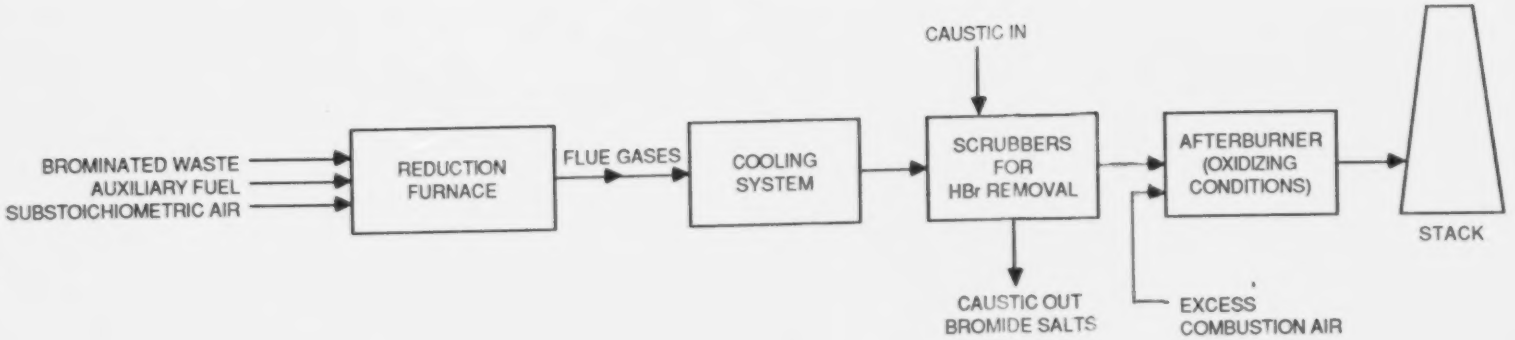


Figure 3-3. Schematic flow diagram for starved-air incineration. (John Zink Co.)

would be incinerated under reducing conditions (less than stoichiometric amounts of oxygen) to convert all feed bromine to hydrogen bromide. The gaseous products of partial combustion would be cooled and passed through a scrubber to remove HBr and other pollutants. The scrubber effluent gases would then be reoxidized in an afterburner to ensure the complete combustion of all organics. The products from the afterburner, which usually consist of carbon dioxide and water, would be released into the atmosphere. If the afterburner products were to contain any toxic pollutants, a secondary scrubbing system would be required to reduce the emissions to acceptable levels.

Cement Kiln

Figure 3-4 presents a typical flow diagram of a cement manufacturing process. The production of cement involves four steps: 1) quarrying and crushing of raw materials; 2) grinding and blending of these materials into feed at proper proportions; 3) calcining the raw materials at extremely high temperatures in a rotary kiln furnace to form clinker (an interim product); and 4) finish-grinding of the clinker, blending it with gypsum, and packaging the finished product. The main ingredient (lime) is processed in the crushing and grinding section before it is calcined in the kiln. The kiln is operated at 2000° to 2300°F. The heat required to carry out the calcination is supplied by burning fuel in the kiln under excess-air conditions. The hot gases from the kiln contain substantial particulates, which are removed by fabric filters or cyclones followed by ESP's. The flue gas processing systems in most cement kilns consist essentially of particulate-removal equipment. Very few facilities use wet scrubbing systems to handle toxic chemical emissions.

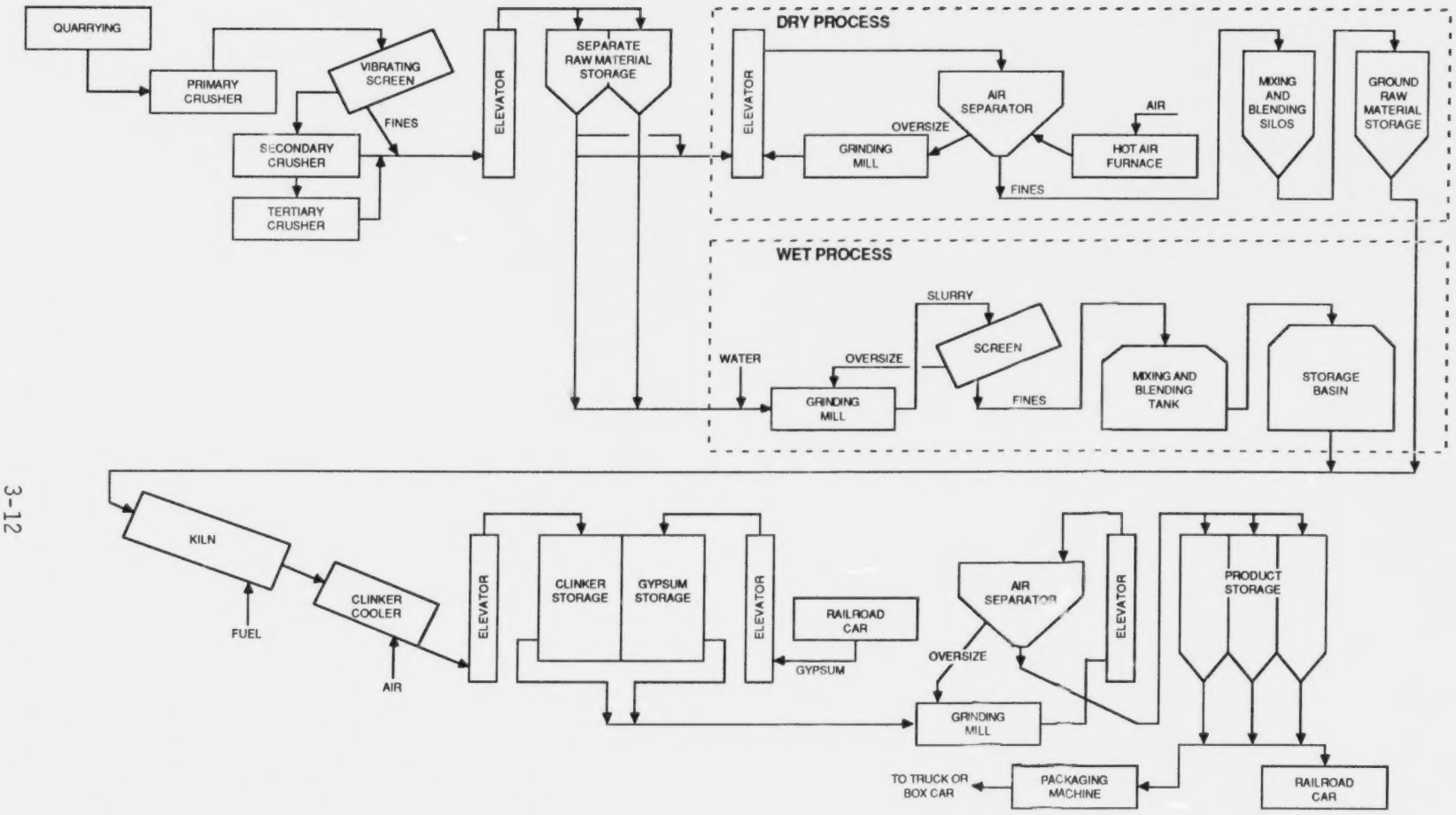


Figure 3-4. Schematic flow diagram for a cement kiln operation.
(PEI, 1982)

The primary cost factor in the production of cement is energy, which accounts for as much as 40 percent of the total cost (PEI, 1987). To offset escalating fuel costs, innovations have been made in the process to reduce fuel usage. One innovation involves the use of hazardous waste fuels; however, not all incinerable waste can be burned in a cement kiln. The most suitable waste is a liquid with high energy value (at least 10,000 Btu/lb), a low water content, and a low concentration of metals (State of California, 1982). Guidelines on the use of hazardous waste in cement kilns have been presented in detail in a report prepared for EPA (PEI, 1987). A growing number of cement kilns are using hazardous waste fuels in their operations. According to a 1981 survey, about 1,000 to 25,000 gallons/day of hazardous waste fuel was being incinerated in cement kilns. Cement kilns have a history of successful incineration of chlorinated waste without any harmful emissions. The hydrogen chloride and chlorine generated in the furnace react with the raw materials (lime and some sodium and potassium in the ore) to form chloride salts. The alkaline conditions in the kiln cause the reactions to be rapid and complete. Thus, the kiln acts as its own scrubber. Further, the formation of salts is advantageous, as it improves product quality. Thus, a substantial incentive exists to use chlorinated waste as fuel. Similar results are expected with brominated wastes. Industry sources believe that under the alkaline conditions prevailing in the kiln, the bromine should react to produce bromide salts, which not only improve the product quality, but also ensure complete destruction without any toxic emissions.

ATEG Process

The ATEG process, developed by the EPA (Rogers and Kornel, 1987), involves a reaction between EDB and sodium hydroxide (NaOH) in the presence of

a phase transfer catalyst, tetraethylene glycol (TEG) to yield acetylene, bromide salts, and water. The reaction products are not toxic and can be easily disposed of. The overall reaction mechanism may be represented as follows:

$$Br\text{-}CH_2\text{-}CH_2\text{-}Br + 2\ NaOH \text{ ------> } CH{\equiv}CH + 2\ NaBr + 2\ H_2O \qquad (5)$$

Potassium hydroxide (KOH) may also be used instead of NaOH as it reacts similarly, although more vigorously (RTI, 1987). Because KOH reacts violently with the carbon tetrachloride (CCl_4) present in the formulations, it creates the potential for a runaway reaction. Therefore, carbon tetrachloride may have to be removed from the pesticide formulations prior to chemical destruction. The reaction has been demonstrated only on a laboratory scale. A comprehensive testing program will be required to demonstrate the process on a pilot scale prior to full-scale operation.

Laboratory-scale studies on this reaction system were carried out by the EPA (RTI, 1987) and the major findings are summarized below:

- The reaction proceeds in two steps, with vinyl bromide as an intermediate product. A very small percentage of the vinyl bromide reacts further in the reactor to yield acetylene. The vinyl bromide had to be treated in a scrubber with the KTEG solution (KOH dissolved in TEG, diluted by water) to achieve complete conversion to acetylene. Thus, the reaction mechanism is as follows:

$$Br\text{-}CH_2\text{-}CH_2\text{-}Br + NaOH \text{ -------> } Br\text{-}CH{=}CH_2 + NaBr + H_2O \qquad (6)$$

$$Br\text{-}CH{=}CH_2 + KOH \text{ ----------> } CH{\equiv}CH + KBr + H_2O \qquad (7)$$

- The reactions are exothermic with an overall heat of reaction of 30 kcal/gmole (RTI, 1987). As per EPA, the reactor temperature should be maintained below 113°F at all times to avoid possibilities of a runaway reaction.

- The reaction seems to have an inception time of about 15 minutes and an overall reaction time of 45 minutes.

- Laboratory tests seem to indicate relatively rapid reaction between the reactants. Hence, gradual feeding of the reaction constituents, especially at high EDB concentrations, is necessary to avoid any rapid runaway reaction.

- Carbon disulfide (CS_2), a constituent of some of the pesticide formulations, has been found to react quantitatively with the ATEG to form a viscous sludge that inhibits the EDB destruction reaction (RTI, 1987).

- Chloropicrin, a major constituent in some formulations, reacts with the catalyst TEG, which inhibits the EDB destruction reaction (RTI, 1987). Moreover, the products of the reaction with chloropicrin are believed to be varied and have not been analyzed as yet.

Thus, to successfully dispose the pesticide formulations, it is important that the constituents which impede the reaction be removed. A common way to do this would be distillation. Distillation of the CS_2 formulations should not be a problem, although distillation of chloropicrin formulations could be difficult. An advantage with distillation is that the products of distillation could be sold at market value and improve the overall process economics.

A schematic flow diagram for this process was developed by the EPA. Based on the various inputs from the EPA, this flow diagram was refined to identify key process equipment (Figure 3-5). The subsequent engineering evaluation has been carried out for the flow scheme identified in Figure 3-5.

The process was proposed to be a batch operation in which each batch treats approximately 300 gallons of pesticide. The EPA has indicated that solid NaOH should be used for this reaction. Solid NaOH flakes would be added to the reactor at a controlled rate using a suitable feeder (e.g., screw feeder). This should help to control the reaction rate and to avoid the possibility of runaway reactions. The reaction between EDB and NaOH produces vinyl bromide gas, sodium bromide, and water. The overall reaction

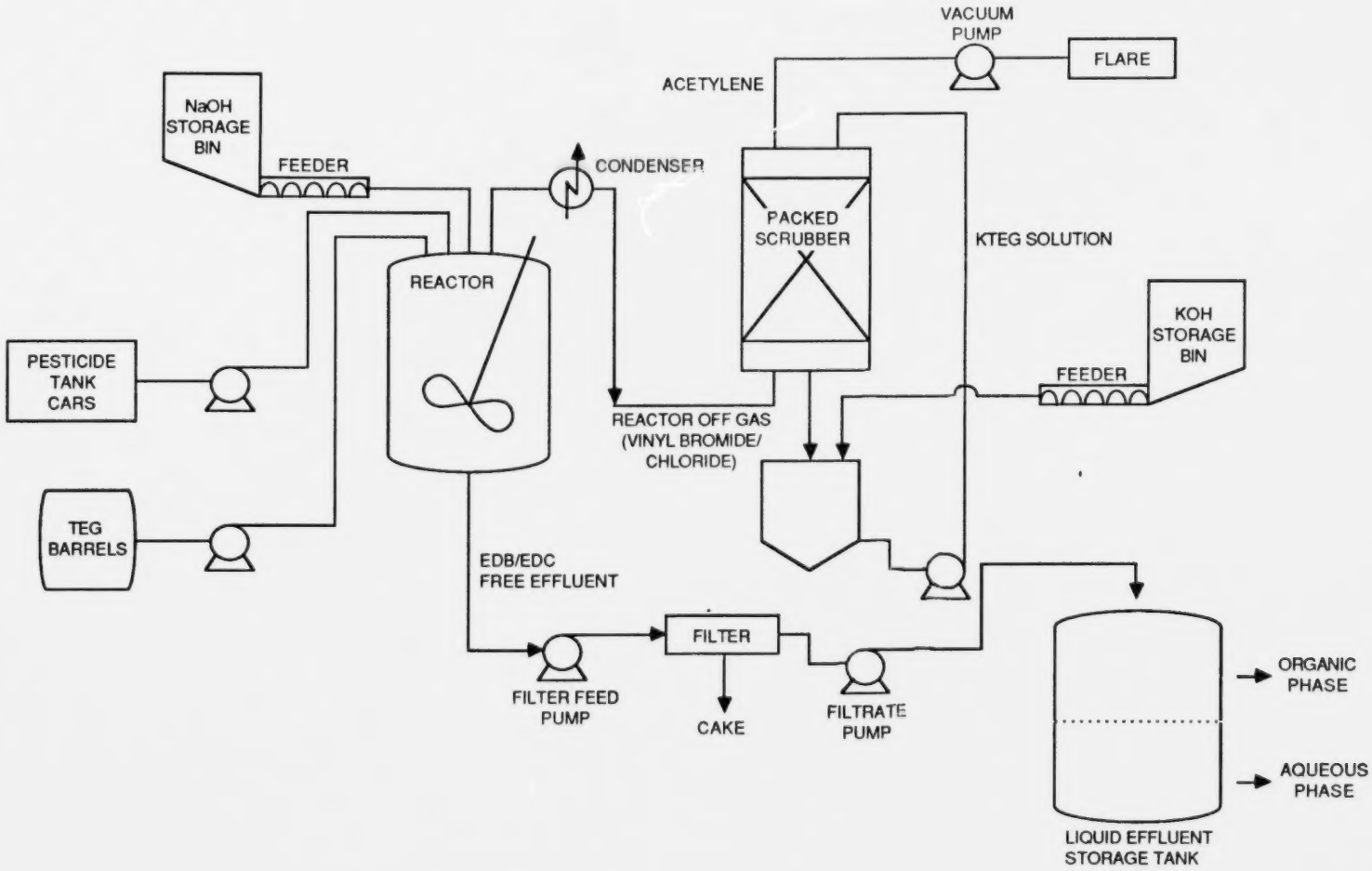


Figure 3-5. Schematic flow diagram for ATEG process.

time would be about an hour. The reactants would be fed at ambient temperature and the reactor temperature would not be allowed to exceed 113°F. The reaction would be carried out in a well mixed jacketed reactor vessel to facilitate efficient heat transfer. An agitator would keep the reactor contents well mixed.

The vinyl bromide formed during the reaction would be treated further with KTEG solution to produce acetylene gas and potassium bromide salt. EPA suggested treating the reactor off gases in a packed bed counter-current scrubber. EPA has proposed the use of Flexipac regular packings in the scrubber. These packings are reportedly self-wetting and efficient in flushing any solids that are formed. Because acetylene is highly explosive, the EPA has suggested that it be removed from the system with a vacuum pump and subsequently flared to produce carbon dioxide and water. The highly water-soluble potassium bromide should dissolve in the KTEG solution, which is about 60 percent water. The KTEG solution contains a large amount of TEG to achieve higher reaction rates. However, since TEG is expensive, discarding the spent solution from the scrubber would make the overall process somewhat expensive. As a result, the EPA has proposed that the liquid effluents from the scrubber would be discharged into a collection tank, with makeup quantities of KOH added directly to this collection tank. The solution would be filtered before it is recycled back to the scrubber. This way, it is believed that the solids formation in the scrubber could be minimized and the solution used for longer periods of time without replenishing it.

The liquid effluents from the reactor contain other organic waste constituents, alkali salts, and water. It is believed that the alkali salts would partially dissolve in the water formed. The undissolved salts would

remain as suspended solids and be removed in a solid-liquid separator (probably a filter). The filtrate would be stored in a tank that would also act as a phase separator. The liquid effluent (from the reactor and scrubber) may be further treated to recover byproducts of value, or it may be treated for ultimate disposal.

Two economic options have been considered for this process. The first involves building a completely new facility with all new equipment. The second involves using some process equipment available at the GARD facility (reactors, flare, and stack) to be used along with some new equipment.

Zinc Process

This process entails a classical organic reaction for the dehydrohalogenation of halogenated organics (Fieser and Fieser, 1967) and was suggested to RTI by Al Kornel of EPA. Metallic zinc reacts with EDB at ambient temperatures to produce ethylene gas and zinc bromide. The reaction is represented as follows:

$$Zn + Br\text{-}CH_2\text{-}CH_2\text{-}Br \text{ ------> } ZnBr_2 + CH_2{=}CH_2 \qquad (8)$$

However, the reaction has been demonstrated only on a laboratory scale. Like the ATEG process, a comprehensive testing program would be required to demonstrate the process on a pilot scale prior to full-scale operation.

Laboratory-scale studies of this reaction have resulted in 99+ percent EDB destruction (RTI, 1987). During these experiments, optimal results were obtained by using 100- to 200-mesh zinc powder slurried in distilled water and a little hydrochloric acid. The acid supposedly cleans the zinc surface and thereby enhances the reaction rate. Slightly more water was added than that required to dissolve the zinc bromide formed in the reaction. The reaction temperature was not allowed to exceed 113°F.

The reaction is exothermic, with very high heat of reaction. It has been suggested that the reaction temperature should be maintained below 113°F to avoid any possibility of runaway reactions.

Preliminary tests with chloropicrin formulations by the EPA resulted in complete destruction of the EDB. However, the reaction with chloropicrin forms a whitish powder (believed to be zinc salts of carbonate or oxide, or hydroxide), which coats the zinc surface and inhibits the reaction with EDB. Unless prevented, this will increase the zinc consumption.

Based on the preceding information, a preliminary flowsheet has been developed for this process (Figure 3-6). The process would be a batch operation. A screw-type feeder would be used to add the zinc particles (approximately 100-mesh) at a controlled rate to the reactor containing the pesticide batch. Appropriate amounts of water and 30 percent hydrochloric acid also would be added to the reactor at a controlled rate. This approach, plus maintaining the temperature below 113°F at all times should achieve a controlled reaction rate. The reactor would be a jacketed vessel equipped with a turbine-type high-efficiency impeller. The reaction gases (primarily ethylene) would require no further processing and thus would be sent directly to the flare. The liquid effluents from the reactor consist of an organic phase and an aqueous phase. Zinc bromide formed in the reaction is highly water soluble; therefore, the only suspended solids would be the unreacted zinc. These solids would be separated in a solid-liquid separator (filter), and the filtrate would be placed in a storage tank, which would also act as a phase separator. The filtrate may be further processed to recover any by-products of value or discharged from the process for disposal.

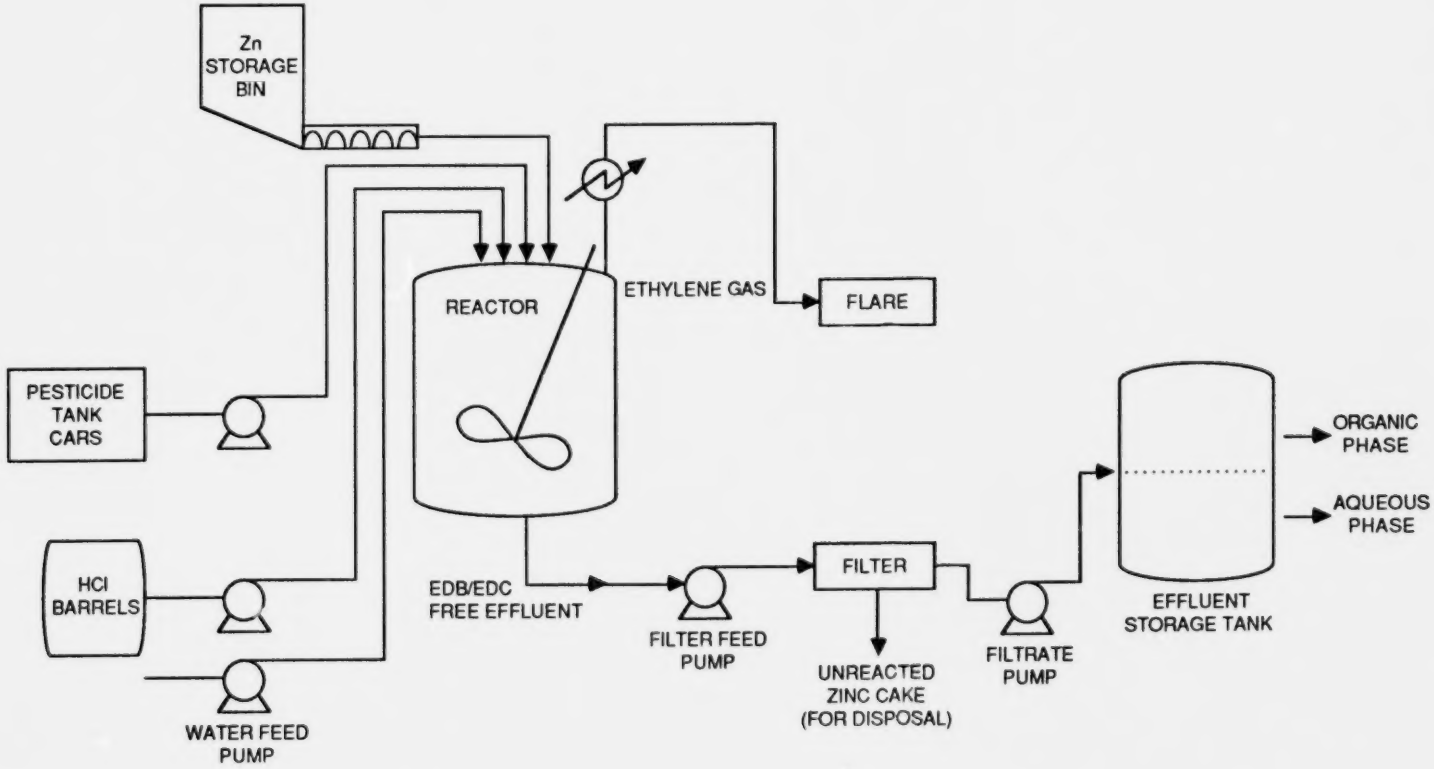


Figure 3-6. Schematic flow diagram for the zinc process.

Two capital investment alternatives are possible for this process. The first alternative entails the construction of a completely new facility with all new equipment. Under the second alternative, some equipment from the GARD facility would be used in conjunction with new equipment.

PROCESSES NOT SELECTED

Williamson's Synthesis

This process involves another classical organic chemistry reaction. This reaction would be suitable to convert methyl bromide (CH_3Br) to dimethyl ether [$(CH_3)_2O$] in the presence of methanol (CH_3OH) and an alkali. Either NaOH or KOH may be used. The reaction is represented as:

$$CH_3Br + CH_3OH + KOH\ (NaOH) \text{ ------> } (CH_3)_2O + KBr\ (NaBr) + H_2O \qquad (9)$$

Methyl bromide is available in liquified gas cylinders; therefore, this reaction can be carried out in some kind of a gas liquid contactor. Because the amount of methyl bromide that needs to be destroyed is very small, a separate process for its destruction was not considered. The applicability of this process for other formulations, including methyl bromide, has been tested on a laboratory scale. However, after discussions with EPA, this process was not reviewed for the proposed application.

MODAR Process

MODAR, Inc., of Houston, Texas, has developed a novel technology for the destruction of hazardous waste that uses the special properties of supercritical water (above 705°F and 3200 psia). The process is based on the principle that water in the supercritical region exhibits properties far different from normal water. The density of supercritical water (SCW) is low enough (0.05 to 0.5 g/ml) and the temperature is high enough to effect the essential

elimination of hydrogen bonding. As a result, the dielectric constant is reduced from 80 to less than 2, and many normally water-insoluble organics become highly soluble. In contrast, inorganic salts become only slightly soluble. The dissolved organics can be oxidized to give CO_2 and water and hetro-atoms (including halogens, phosphorus, sulfur, and metals) are precipitated as salts.

The process consists of the following steps:

1) The toxic or hazardous waste is slurried with makeup water to provide a mixture of about 5 to 10 percent by weight. The slurry is pressurized and heated to supercritical conditions to avoid char formation. Heating is attained by mixing the feed with superheated SCW, which is generated in a subsequent step. During a short residence time in the tube leading to the oxidizer, organics in the feed are converted to combustible gases, low to intermediate molecular weight compounds (furans, furfurals, alcohols, aldehydes), and inorganic salts.

2) Air or oxygen and an alkali solution are pressurized and mixed with the feed. Because the water is still supercritical, the oxidant is completely miscible with the solution (i.e., the mixture is a single, homogeneous phase). Organics are oxidized in a controlled but rapid reaction. Because the oxidizer operates adiabatically, the heat released by combustion of readily oxidized components is sufficient to raise the fluid phase to temperatures at which all organics are oxidized rapidly. For a feed of 5 percent organics by weight, the heat of combustion is sufficient to raise the oxidizer effluent to at least 1022°F. The hetro-atoms (like halogens) react with the alkali to form inorganic salts.

3) The effluent from the oxidizer is fed to a salt and sediment separator, where inorganics and sediments originally present in the feed are removed as a solid slurry. At 932°F and above, the solubility of inorganics in SCW is extremely low.

4) A portion of the superheated SCW is recycled to an eductor upstream of the SCW oxidizer. This operation provides for sufficient heating of the feed to bring the oxidizer influent to supercritical conditions.

5) The remainder of the superheated SCW (with some CO_2 and N_2) is available for power generation or use as high-pressure steam. A portion of the available energy is used to generate the power required to pressurize feed and oxidant. The energy required to pressurize the oxidant is recovered in the expansion of the products of combustion in the superheated SCW turbine.

As a waste destruction process, the MODAR concept has the following advantages:

- The process is carried out in a closed system, which allows total physical control of waste material to be maintained from storage through reaction and final discharge of products.

- The process has a high destruction efficiency (DRE). Two liquid PCB wastes treated by this process at the CECOS facility in Niagara Falls, New York, under permits, showed 99.999 percent DRE (Staszak et al. 1987). The process apparently gave similar DRE's for other wastes when tried on a bench scale.

- The process can be adapted to a wide range of feed mixtures and scale of operations. No preprocessing of the waste is required; therefore, this process may be able to destroy all the waste pesticides without a need for distillation.

- Skid-mounted, transportable systems are being designed along with large-scale stationary units. With a transportable unit, the need to transport all the hazardous waste to a fixed site would be eliminated, which would make the operation safer and more economical.

The use of this process also has the following disadvantages:

- No operational units are currently in the field. It would take a year to set up a unit that could take care of this waste. Thus, it does not fit in with the time frame required by the EPA.

- The process operates under very high pressure (above 218 atms). In the past, other wet oxidation processes have had problems and experienced explosions. The risk of an explosion is quite high.

- The current design could treat 20,000 gallons/day of the 10 percent organic mixture. The design is still in the study phase, so any process deficiencies which may emerge in scaleup are still unknown.

- Because this is a very sophisticated technology, more highly skilled operators would be required to operate the process as compared to other processes. Thus, operational costs could be substantially higher than for other processes operated by less-skilled labor.

- No data are available on destruction of brominated waste, even on a bench scale. A bench-scale characterization was quoted for $25,000. Also, because MODAR is primarily an oxidation process, bromine will be formed in the reactor. In incinerators, scrubbing bromine with an alkali is very difficult, and bromine removal with an alkali may not be easy, even in the MODAR process.
- MODAR is not interested in facility operation; their interests lie in designing and selling units to others. Thus, EPA might have to

buy the equipment. Even if MODAR decided to do the job for EPA, the EPA would have to provide land, site preparation, permitting, etc. This option could turn out to be very expensive. Nevertheless, if the unit could be used for destroying other wastes (assuming it can work as a regular waste treatment facility), the marginal cost for destroying the waste could range from $3 to $4/gallon (excluding the cost of permits, site preparation, and installation).

After the advantages are disadvantages were weighed, it was decided to eliminate this process from further consideration.

SECTION 4

EVALUATION OF TECHNOLOGIES

This section presents the results of the technical evaluation of each of the available options for destroying pesticide formulations. This evaluation consisted of a literature review, an engineering assessment and supportive calculations, and study cost estimates. Each potential candidate process was reviewed critically with respect to each of the selection criteria introduced in Section 2. Table 4-1 summarizes the results of the evaluation with respect to the selection criteria for each of the processes.

THERMAL DESTRUCTION

All options discussed under thermal destruction in Section 3, except the cement kiln, involve the use of a commercial incineration facility. As discussed in Section 3, these alternatives differ only with regard to the process conditions maintained in the incinerator. All of the operating conditions required to achieve successful destruction of hazardous waste are possible in a commercial incinerator.

The options for which a commercial incineration facility is suitable are as follows:

1) Incineration in oxidizing atmosphere--conventional incineration
2) Incineration in the presence of SO_2 or sulfur-containing wastes
3) Starved-air incineration

TABLE 4-1. SUMMARY OF RESULTS OF ENGINEERING EVALUATION

Criteria	Incineration in presence of sulfur wastes	Starved air incineration	Cement kiln	ATEG	Zinc process
Status	Commercial.	Not yet demonstrated.	Commercial.	Pilot plant. (Bench scale for EDB application).	Bench scale.
Accessibility	Accessible. Rollins has offered this technology.	Accessible. At least two facilities interested in pursuing this option.	Accessible. Two companies interested.	New plant to be built or existing plant to be modified.	New plant to be built or existing plant to be modified.
Past Experience	Trial burns at Rollins, Deerpark, TX, facility resulted in EDB destruction efficiencies greater than 99.9999%. There were no visible bromine emissions at the stack. Preliminary results show that all bromine fed to the incinerator is captured in the scrubber system.	None for brominated waste.	One known test in Canada. Reports almost complete capture of bromine in the process residue.	Limited to bench scale demonstration.	Limited to bench scale demonstration.

(continued)

TABLE 4-1 (continued)

Criteria	Incineration in presence of sulfur wastes	Starved air incineration	Cement kiln	ATEG	Zinc process
Need for Development and Testing	In light of the successful trial burn, it is believed that no further development or testing is required.	The chemistry of bromine/HBr favors formation of bromine over HBr at ordinary operating conditions. Theoretically, this equilibrium can be shifted to yield HBr by reducing the oxygen and increasing the water vapor content. However, under partial pyrolysis, the extent of improvement in HBr formation is not known.	Minor modifications to kiln feed required. Process chemistry favors bromine capture in product without major changes in kiln design.	The development status of this technology will require more pilot scale testing to establish feasibility, optimum operating procedures, and process parameters for design and scale-up.	The development status of this technology will require more pilot scale testing to establish feasibility, optimum operating procedures, and process parameters for design and scale-up.
Pre-processing	Routine.	Routine.	Routine.	Carbon disulfide interferes with ATEG reaction. This will have to be removed by distillation. Chloropicrin may be difficult to treat with ATEG, and is not distilled easily. Thus,	Carbon disulfide interferes with the zinc reaction. It will have to be removed by distillation. Chloropicrin produces a coating on the zinc and may have to be removed by pre-processing.

(continued)

TABLE 4-1 (continued)

Criteria	Incineration in presence of sulfur wastes	Starved air incineration	Cement kiln	ATEG	Zinc process
Pre-processing (continued)				chloropicrin-containing formulations may have to be disposed of independently.	
Process Safety	Safe.	Safe.	Safe.	Acetylene is a major product of the process, which poses an explosion hazard. Also reaction is highly exothermic requiring careful control.	Ethylene and hydrogen are major reaction products, increasing explosion risks. Reactions are very exothermic requiring effective monitoring and and control to avoid run away reactions.
Toxic Emissions	None, based on trial burn results.	Bromine emissions are possible.	Possibility of bromine emissions and partially oxidized organics.	Vinyl bromide and chloride emissions are possible.	Ethylene is reportedly herbicidal.

(continued)

TABLE 4-1 (continued)

Criteria	Incineration in presence of sulfur wastes	Starved air incineration	Cement kiln	ATEG	Zinc process
Residues	Brominated scrubber solution and sludges will require careful handling.	Brominated scrubber solution and sludges will require careful handling.	No problems envisioned.	Reactor effluents may be classified as a hazardous waste which will require appropriate handling and disposal. The residue contains byproducts of value which may be recovered prior to disposal.	Reactor effluents may be classified as a hazardous waste which will require appropriate handling and disposal. The residue contains byproducts of value which may be recovered prior to disposal.
Need for New/ Additional Equipment	None.	New facility needs to be built or existing one modified.	None.	Build new facility or modify existing one.	Build new facility or modify existing one.
Extent of Corrosion	Corrosivity will be greater than that of chlorine, which is handled in existing facilities and, hence, may be a concern.	Corrosivity will be greater than that of chlorine, which is handled in existing facilities and, hence, may be a concern.	Due to the alkaline conditions in the kiln, corrosion is not expected to be a major problem.	Stainless steel material of construction is believed to be adequate. However, suitability of using SS needs to be established. FRP	Assuming that the problem of zinc coating (for chloropicrin formulation) can be solved without using excess HCl, there should be no

(continued)

TABLE 4-1 (continued)

Criteria	Incineration in presence of sulfur wastes	Starved air incineration	Cement kiln	ATEG	Zinc process
Extent of Corrosion (continued)				lined material could be a possibility.	problem of corrosion. However, if high acid consumption is required to clean-up the zinc surface, then corrosion could be a major concern.
Process Compatibility with Pesticides	Compatible.	Compatible.	Compatible.	Carbon disulfide in the formulations is incompatible with the TEG catalyst, which inhibits the main dehalogenation reaction.	Carbon disulfide reacts with zinc and will have to be removed to reduce high operating costs.
Secondary Environmental Impact On Health Considerations	Bromine emissions of 0.1 ppm are known to be a health hazard. However, test burn results indicate no bromine emissions.	Bromine emissions of 0.1 ppm are known to be a health hazard.	Bromine emissions of 0.1 ppm are known to be a health hazard. In addition, secondary impact and and health hazards can arise due to POHC's.	Possible due vinyl bromide and chloride emissions. Both are known to be carcinogenic compounds.	Possible due to volatile organics from reaction mixture. Ethylene is known to affect plants and vegetation.

(continued)

TABLE 4-1 (continued)

Criteria	Incineration in presence of sulfur wastes	Starved air incineration	Cement kiln	ATEG	Zinc process
Mechanical Reliability	Reliable.	Reliable.	Reliable.	Reliable.	Reliable.
Transportational Acess to Facility	Available.	Railroad access available at some facilities. Mobile incinerators are available.	Railroad access available at at least one willing facility.	To be determined.	To be determined.
Storage and Handling of Pesticide and Residue.	No problems envisioned.	No problems envisioned.	No problems envisioned.	No problems envisioned.	No problems envisioned.
Cost	Approximate range is 50 to 80 cents/lb.	Unknown.	Approximately $0.76-$1.3/lb.	$0.34 to $0.78/lb[a]	$0.3 to $0.50/lb[b]
Permitting	Some facilities may require modification for EDB. Others may need to have new permits. Still others have the appropriate permits.	New permits would be required.	Permit modification required.	New permits or modifications required.	New permits or modifications required.
Probability of Success	Excellent. Incineration in presence of sulfur dioxide shows excellent promise.	Fair. Test burns would be required to judge performance.	Good. Test burns would be required to judge performance.	Good. Pilot scale testing required to establish feasibility	Good. Pilot scale testing required to establish feasibility and

(continued)

TABLE 4-1 (continued)

Criteria	Incineration in presence of sulfur wastes	Starved air incineration	Cement kiln	ATEG	Zinc process
Probability of success (continued)	Results of a recent test burn show no bromine emissions at the stack and DREs greater than 99.9999% for all POHCs.			and optimum operating conditions.	optimum operating conditions.
Time Schedule for Completion	6 months or less.	Approximately 1½ to 2½ years.	Depends on allowable feed. Approximately 1½ years.	Approximately 2½ years.	Approximately 2½ years.

[a] Cost excludes the cost for permitting, disposal of chloropicrin stock, and land lease. Also, since steam, water, and compressed air requirements are minimal, their contribution to operating cost was considered negligible. The amount of pesticide treated excludes the amount of chloropicrin formulation. Also, these cost figures are exclusive of development costs.

[b] Cost has been calculated assuming that the problem of zinc coating with chloropicrin formulations can be solved without adding excess hydrochloric acid. Also, cost excludes the cost of permitting and land lease. Since steam, water, and compressed air requirements are minimal, their contribution to operating cost was considered negligible. The amount of pesticide treated includes the total amount of pesticide that needs to be destroyed. Also, these cost figures are exclusive of development costs.

Because all of the preceding options use essentially the same process design configuration, they are reviewed under one major option--destruction of pesticide waste in a commercial incineration facility. Differences arising from the varying modes of operation are highlighted whenever relevant. Thermal destruction in a cement kiln is reviewed separately.

Incineration in a Commercial Incinerator

Status and Accessibility--

All of the options appear to be easily accessible, as indicated in the following subsections.

Incineration in oxidizing conditions--This technology for the incineration of hazardous waste has been commercialized and is currently in operation in numerous facilities nationwide. In fact, some of these facilities (IT, VESTA, and ENSCO) offer mobile incineration systems, which can preclude the need for transporting the hazardous waste. Most of these facilities have a history of successful handling of hazardous wastes, and a few of them also claim to have handled pesticides. During this evaluation, PEI contacted several of these facilities to determine their interest in performing this service and to gain their perspective on the applicability of the technology to handle brominated waste. At least seven such facilities [VESTA, SHIRCO, ENSCO (only if the operation can last more than a month), IT, Chemical Waste Management, Rollins, and John Zink] indicated an interest in doing this work.

Incineration in the presence of sulfur dioxide--At least one commercial facility in Europe is using this technology successfully for halogenated wastes. Rollins Environmental is currently planning to use this technology for the present application.

Starved-air incineration--International Technology Corp. and John Zink have expressed an interest in trying this option in addition to others. John Zink has a design for a starved-air incinerator which could be used for EDB application.

Past Experience--

Incineration in an oxidizing atmosphere--This is the standard mode of operation for all commercial facilities. Many facilities are experienced in the incineration of chlorinated wastes; however, few, if any, have had experience with brominated wastes. The problem associated with destroying brominated wastes in excess-air incineration is not one of achieving the necessary destruction efficiencies; rather, it concerns containment of the undesirable bromine (Br_2) emissions. The literature indicates that the bromine sinks in water and forms an irritating brown vapor (U.S. Coast Guard 1984). One facility (John Zink) reported the formation of a fog in the scrubber caused by bromine, which resulted in a substantial reduction in scrubber efficiency (J. Cegielski, personal communication with EPA). Most of the bromine escaped into the atmosphere. Thus, conventional incineration of brominated waste might generate bromine emissions.

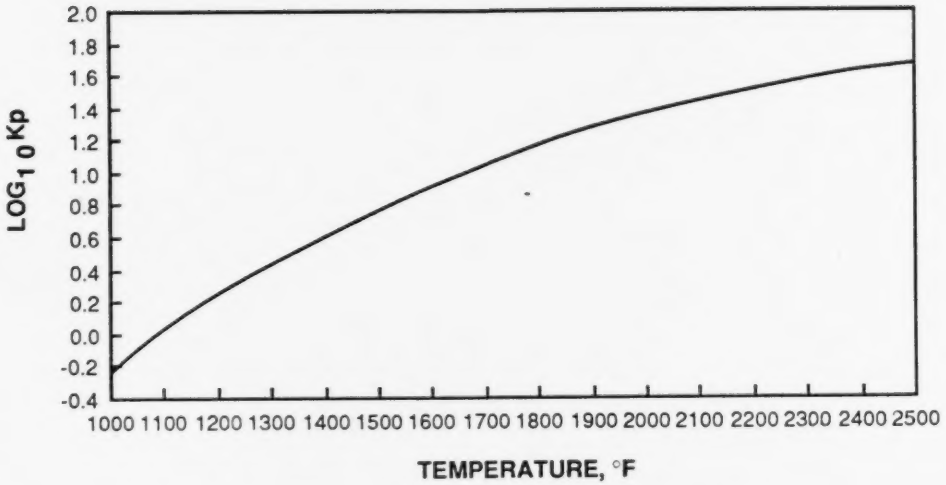
On the other hand, it has been suggested that hydrogen bromide (HBr) can be scrubbed efficiently in existing scrubber systems. If an incinerator can reduce bromine to HBr, the use of commercial incinerators may be a viable option for destroying pesticide formulations. The bromine/HBr thermodynamics, however, favor the formation of bromine under incinerator operating conditions (Eicher, Cudahy, and Troxler 1985). The equilibrium reaction is as follows:

$$Br_2 + H_2O \rightleftharpoons 2\ HBr + 1/2\ O_2 \qquad (10)$$

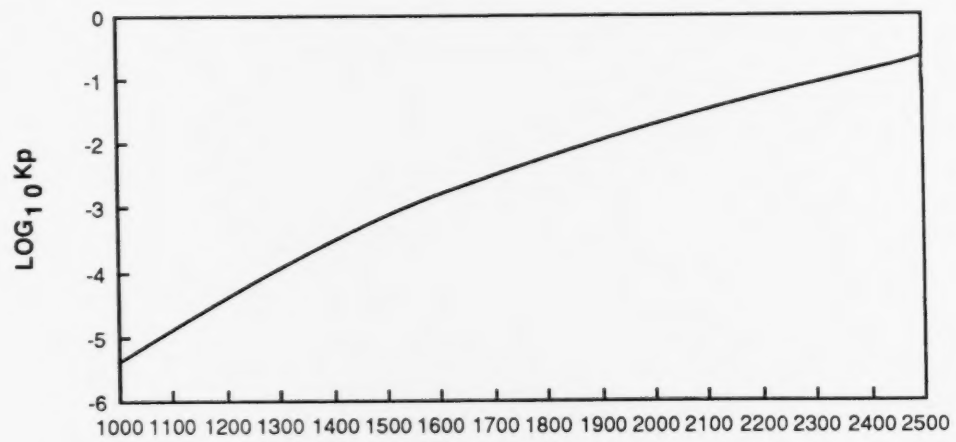
Figure 4-1 shows in separate plots the equilibrium constant Kp against temperature for chlorine and bromine. At 1800°F, the equilibrium constant for bromine is about 5.9×10^{-3}, as opposed to 12.5 for chlorine. The result is almost total bromine formation in the incinerator. A study by Eicher, Cudahy, and Troxler (1985) indicates about 75 percent of the bromine goes to Br_2 in a typical incinerator. Thus, preferential formation of HBr in the incinerator is possible only if the operating conditions are changed to favor HBr formation thermodynamically or if the bromine is made to react with some other reagent in situ to produce HBr. The former can be achieved by starved-air incineration, whereas the latter can be achieved by reacting the Br_2 formed with SO_2 to form SO_3 and HBr.

Incineration in the presence of SO_2--This process modification of conventional incineration is currently being operated successfully at an incineration facility of Bayer, Germany. This facility has been in operation since 1977 and reportedly has incinerated halogenated wastes, "to a degree where not even traces of halogen can be identified by analysis" (Fabian, et al., 1979). In the United States, the only company claiming to have substantial experience with brominated wastes is Rollins Environmental. Recently, EPA conducted a test burn of the EDB formulation at the Rollins, Deer Park, Texas, facility. The important results of the test burn (Alliance Corp., 1988) are as follows:

- DREs for the three POHCs (EDB, EDC, and CCl_4) easily met the "four nines) RCRA requirements. The destruction of EDB in particular was greater than 99.9999 percent.
- There were no visible bromine emissions at the stack.
- Continuous emissions monitoring data for CO_2, O_2, NO_x, and SO_2 meets the required standards.
- All organic bromine fed to the system reportedly exits the system through the scrubber water stream.



Equilibrium Constant (Kp) Curve for HCl/Cl_2



Equilibrium Constant (Kp) Curve for HBr/Br_2

Figure 4-1. Equilibrium constant Kp against temperature for chlorine and bromine (Eicher et al. 1985).

Four Nines (1987) have reported similar observations during incineration of iodine. Thus, this option seems to have excellent capability to successfully destroy the EDB formulations.

Starved-air incineration--There is no known experience of destroying hazardous waste with this technology. However, personal communications of Mr. John Cegielski, John Zink Co., with EPA indicate that John Zink has a design for this process which could be used to eliminate the brominated waste.

Need for Development--

The preceding discussion points up an obvious need for development to solve the problem of bromine emissions. This problem can be handled in two ways:

1. Modification of the process, which would involve some change in the process conditions to obtain preferential conversion of all the bromine to HBr.

2. Modification of the scrubber design or operation to obtain successful removal of all the bromine from the flue gases.

Under the first choice, the most viable options are incineration in the presence of sulfur dioxide and starved-air incineration (partial pyrolysis).

Incineration in the presence of sulfur dioxide--Results of the recent test burn at the Rollins, Deer Park, Texas, facility show that destruction of EDB formulations is complete and meets all the necessary standards regarding DREs and emissions. Thus, it is believed that no further development is required for this process.

Starved-air incineration--The chemical equilibrium for the Br_2/HBr system is represented by Equation (10). The equilibrium constant is given by:

$$Kp = \frac{[HBr]^2 [O_2]^{\frac{1}{2}}}{[Br_2] [H_2O]}$$

Thus, it is theoretically possible to shift the equilibrium in favor of HBr by:

1. Operating the furnace at the highest possible temperature so as to obtain the highest equilibrium constant (refer Figure 4-1).
2. Operating the furnace at low oxygen concentrations (less excess air). In fact, if the oxygen concentrations could be reduced to zero, almost all of the bromine will form HBr.
3. Operating the furnace at high water partial pressures which ensures the availability of hydrogen for the reaction to form HBr.

However, in most commercial facilities, due to their present design and operation (Four Nines, 1987), it may not be possible to operate the auxiliary burners at high temperatures and high water ratio. Moreover, most commercial facilities use kilns which operate at lower temperatures. Equilibrium calculations under the typical operating conditions that would prevail in a commercial incinerator, operated under starved-air conditions (Appendix A), indicate that a substantial amount of Br_2 would still be formed because of the very low value of the equilibrium constant Kp. A considerably more significant question, however, concerns the change of equilibrium as the furnace gases are cooled to approximately 200°F before they enter the scrubbing system. The equilibrium gas composition should be calculated at this temperature, rather than in the furnace. The lowest temperature at which the Kp value for the Br_2/HBr system is available is about 1000°F. The Kp value decreases rapidly with decrease in temperature; hence, it may be expected to be much lower than that at 1000°F. Equilibrium calculations at 1000°F (Appendix A) indicate almost complete bromine formation. Thus, as the gases enter the scrubber, most of the HBr would have been converted to Br_2 and the situation would be no better than that which occurs during conventional,

excess-air incineration. Thus extensive testing will be required to establish the feasibility of this option. Moreover, the literature indicates that halogenated wastes are not likely candidates for the starved-air incineration (Bonner et al. 1981).

Conventional incineration--If modifying the process in the incinerator operation is not a desirable alternative, or if such modifications fail to produce the desired results, the scrubber section may offer a solution. It has been suggested that an efficient scrubber design is a must for halogenated waste incineration, and packed towers or plate columns have been recommended for this purpose. Although venturi scrubbers may be used in a few cases, they do not offer a desirable alternative, as they do not provide good gas-side mass-transfer characteristics. Even with efficient scrubbers, removing bromine from the flue gases will be a difficult task. Some of the process modifications that might be successful are as follows:

1. Sulfur dioxide can be mixed with the incinerator exit gases and the mixture absorbed in water with very dilute amounts of sulfuric acid in a packed column. D. van Velzen et al. (1978, 1979, 1980) found this method to yield almost complete conversion of bromine and SO_2. Two studies present relevant details on the mass-transfer characteristics and design parameters (D. van Velzen et al., 1978, 1979). The experimental data presented in these two studies indicate a good potential for this mode of operation. Nevertheless, a test run would be desirable to test the efficacy of this modification and to determine any associated operational problems.
2. The other option involves the use of an efficient solvent that can readily absorb bromine. Solvents that can undergo rapid reaction with bromine are preferable. Some suggestions include ammonia solution, caustic solution, and lime slurry. No data are currently available on the performance of these solvents; however, it is interesting to note that ammonia is recommended for containment of bromine spillage. Thus, ammonia solution may be a worthwhile consideration.

In conclusion, a few options hold promise; however, the data base is too sparse to predict the extent of success or the approximate costs entailed.

Trial burns are almost imperative for assessing the feasibility of the available options.

Other options--One of the options suggested by the IT Corporation involves the introduction of caustic solution in the combustion chamber. The idea is to react the bromine in situ. This option will provide a homogeneous phase reaction between the alkali and bromine, and the reaction rates could be high. It also provides a longer residence time for the gases with the alkali to achieve the necessary levels of reaction (removal). Thus, this may be a possible area for development.

General Criteria--

The criteria presented in the following subsections are applicable to all modes of operation.

Need for additional equipment--All the incineration options considered in this discussion involve the same basic process design configuration and equipment, and all can be performed in an existing commercial facility. For some options, additional equipment or components may be needed to adapt an existing system for any of the process operations. A good corrosion-resistant refractory lining would be needed in the furnace, and the flue gas ducting may have to be made of fiberglass-reinforced plastic (FRP). The scrubber system also may have to be refractory-lined or Teflon-lined for corrosion resistance. Specific modifications, if any, required for starved-air incineration are unknown. Incineration in the presence of SO_2 does not appear to require any modifications.

Toxic emissions and secondary environmental impact--It is evident from the previous discussion that incineration in the presence of sulfur-containing

waste or SO_2 does not pose any problem of toxic emissions. However, the potential for possible toxic emissions and secondary environmental impacts due to bromine and HBr emissions for all other modes of incineration is evident from the preceding discussion. Secondary environmental impacts may arise from the possibility that these compounds can enter the water intake system and thereby pose a danger. Both compounds, especially bromine, are known to be harmful to aquatic life.

In addition, the starved-air incineration option could emit partially oxidized organics, which may be carcinogenic and very harmful.

Compatibility--The process is compatible with the constituents of the pesticide formulations.

Residues--The brominated scrubber solution and sludges will require careful disposal. In addition, residues from starved-air incineration may contain significant amounts of partially oxidized organics, which will have to be carefully handled or destroyed.

Safety and health hazards--When bromine comes in contact with the skin, it can cause acne and slow-healing ulcers. Inhalation can cause severe irritation of respiratory passages and pulmonary edema. A brief exposure to 1000 ppm may be fatal. The TLV for bromine is 0.1 ppm, and the short-term inhalation limit is 0.4 ppm for 30 minutes. Indications are that bromine cannot be tolerated even at low concentrations. Odor threshold and IDLH for bromine are 3.5 and 10 ppm, respectively (U.S. Coast Guard 1984).

Inhalation of HBr causes severe irritation of the nose and upper respiratory tract and lung injury. Skin contact can result in irritation and burns. The TLV for HBr is 3 ppm; the IDHL value is 50 ppm (U.S. Coast Guard 1984).

Unfortunately, no one knows the ambient concentration levels at which these compounds can have a pronounced health effect, and no regulations on the allowable emissions for bromine have been established. Only four states are currently in the process of promulgating regulations for HBr (RTI, 1987). As a result, the extent of removal efficiencies required at the scrubber outlet cannot be quantified.

Another aspect of safety and health concerns the workers at the incineration facility. Because most of the constituents of the waste are extremely hazardous, operators may have to be equipped with safety equipment such as goggles, self-contained breathing apparatus, and rubber overclothing (including gloves).

Assuming that the problem of emissions can be solved with some process modification, the incineration process is safe. The flue gas would then consist mainly of carbon dioxide and water, both of which are harmless. When properly operated, this process poses little possibility of explosion. Several commercial incinerators are now operating nationwide. Also, incineration is unlikely to generate any solid or liquid residues that would be hazardous and could not be handled in a routine manner.

Transportation access to facility--Among those commercial facilities that are interested in undertaking this task, IT, VESTA, ENSCO, and SHIRCO have transportable units that can be set up at the worksite. Rollins and Chemical Waste Management are known to have railroad access at their facilities; it is believed that John Zink also has railroad access.

Storage and handling of waste--Another aspect of plant safety and toxic emissions concerns the handling and storage of the hazardous waste. The

possibility of spillage and emissions is at a maximum during these activities. Because most commercial incineration facilities handle hazardous wastes on a regular basis, they are believed to have well-designed storage and handling facilities. Most of the constituents of the waste under consideration [e.g., EDB, ethylene dichloride (EDC), chloropicrin] are extremely hazardous and warrant the use of special precautions in their handling. As a part of an incineration program, a comprehensive spillage-control action plan should be prepared, and all operators should be trained to implement it. If attention is given to these items, it is believed that the handling facilities available at existing incinerators should be capable of dealing with pesticides.

Preprocessing--Because of the small quantity of the waste that needs to be destroyed, it may be blended with other wastes before incineration. Care should be exercised to make sure that the pesticide constituents are compatible with other chemicals in the blend.

Corrosion and mechanical reliability--Bromine and HBr are highly corrosive to most metals (U.S. Coast Guard 1984). Bromine is also known to have a corrosive effect on the refractory lining in the furnace. No data are currently available on the extent of corrosion due to bromine and HBr in an existing incineration facility; however, most commercial facilities are designed to handle hydrogen chloride (HCl), which is also extremely corrosive. Comparative data on the corrosivity of bromine/HBr and HCl are unavailable; hence, corrosion could be a potential problem. Industry sources, however, have indicated that the existing material of construction should be able to withstand any corrosive attack due to bromine/HBr. Reportedly, one facility in Europe had major corrosion problems on parts in the gas processing sections that were made of Hastelloy C (Fabian, Reher, and Schoen 1979). These

problems could be solved by the use of Teflon, FRP, or high-quality refractory bricks. Thus, the mechanical reliability of the equipment involved is directly related to the corrosion resistance of the material of construction used. Inasmuch as operating incineration facilities have had extensive experience with chlorinated wastes, these facilities are assumed to be reliable mechanically.

Cost--The costs quoted by vendors during preliminary discussions ranged from 50 to 80 cents/pound of waste; however, these costs could change as the vendors gain a better grasp of the modifications/complexities involved in the process. Cost breakdowns for each operating option are currently not available. However, EPA has proposals from Rollins Environmental and John Zink for this job. Rollins will use SO_2 incineration technology, and John Zink has proposed the use of starved-air incineration.

Permits--Most of the facilities contacted did not have permits to handle pesticides. Some of the newer facilities (VESTA, IT) have permit applications pending for the handling of hazardous wastes. A few facilities (Rollins and Chemical Waste) have indicated that they have permits for handling pesticides which may or may not need modification to include the handling of EDB. Rollins may not require the permit modification.

As mentioned earlier, many commercial incineration facilities were contacted for their input. Appendix C summarizes the information obtained from most of these facilities.

Probability of Success--As reported earlier, the option of incineration in the presence of SO_2 has been successfully demonstrated for EDB destruction during a test burn at the Rollins, Deer Park, Texas, facility. The incineration meets all the required standards for DREs and emissions. Moreover, this

option is reportedly in operation at a Bayer facility in Germany with success, to eliminate halogen emissions during incineration. Thus, incineration in presence of SO_2 holds excellent promise to destroy the EDB formulations.

As regards other incineration options, trial burns will be required to demonstrate their capabilities, although both conventional incineration and starved-air incineration appear to present some significant problems.

Time Schedule--Presently, test burns for incineration in the presence of SO_2 have been completed successfully. Preliminary test results indicate that this option can successfully eliminate the EDB wastes. Moreover, Rollins has obtained a permit to handle pesticides that does not even require modification for EDB. Thus, this option should be able to be used to dispose of all EDB formulations within six months or less.

ADDITIONAL INCINERATION OPTION

Another option for eliminating the EDB waste, which has not been considered in this evaluation, has been suggested by Four Nines, Inc. (1987). Information obtained from Four Nines (Four Nines, 1987) indicates that the conditions necessary to change the Br_2/HBr equilibrium in favor of HBr (discussed under starved-air incineration) can be obtained by using a high intensity burner design (Trane Thermal, John Zink) fired into a liquid injection incinerator. These incinerators can operate at low excess air (0 to 1% excess air), high temperatures and high water content. The EDB would be injected through a steam atomizer along with auxiliary fuel to maintain the combustion temperature above 2400°F. Water injection nozzles (combined with EDB or adjacent to EDB nozzle) would be used to provide high water vapor content in the combustion gases to drive the equilibrium in favor of HBr formation. The off gases would be subjected to an adiabatic quench followed by

conventional scrubbing. This operating scheme is believed to have been implemented successfully with chlorinated compounds. Four Nines believes that this scheme should be able to handle the problem of bromine emissions. However, they recommend prior testing in a pilot or a commercial facility that has a high intensity combustor to establish the performance capabilities. According to Four Nines such burners are available at Trane Thermal pilot plant, John Zink pilot plant, ENSCO, Chemical Waste Management (Chicago) and Rollins Environmental.

Cement Kiln

Status and Accessibility--

A number of cement kilns now in operation incinerate hazardous wastes under the Hazardous Waste Fuels Program. Two kilns, Dundee Cement Co. and La Farge Cement Co., have shown an interest in the incineration of delisted pesticides. Thus, the technology is accessible.

Past Experience--

Cement kilns have been burning chlorinated waste fuels as part of the ongoing Hazardous Waste Fuel Program. When waste lubricating oils containing an average of 0.15 percent bromine were burned in a dry cement kiln at the St. Lawrence Cement Company in Ontario, about 99.3 percent of the bromine in the feed stream was reportedly captured in the pelletized dust, and some bromide was captured in the clinker (Berry 1975). The percentage of bromine in the pesticides, however, is substantially higher. No further test or operating data on incineration of brominated waste in a cement kiln were available. Cement kiln operators, however, believe that brominated wastes will present no new problems.

Need for Development--

Despite a history of hazardous waste incineration in cement kilns, the burning of halogenated wastes has been limited to those containing chlorides. Cement kilns are ideal for burning chlorinated wastes because, in proper quantities, chlorides enhance product quality by combining with the potassium and sodium that might be present in the ore. Further, the alkaline characteristics of the kiln atmosphere abate hydrogen chloride emissions. In essence, the kiln is its own scrubber. Kiln operators expect the bromide waste to act similarly. Because most cement kilns operate without wet scrubbing systems, however, toxic gases from the kiln exit into the atmosphere. Trial burns are therefore required to ascertain the extent of bromine removal and whether additional scrubbing capacity is needed.

Need for Additional Equipment--

Cement kilns are equipped with systems for the control of particulate emissions. Those that burn hazardous waste fuels are scrutinized even more closely to ensure that particulate emissions are minimized. Therefore, the existing facilities should be well equipped to handle particulate emissions. As mentioned earlier, however, most facilities do not have gas treatment systems (chemical treatment). If the flue gas were to contain substantial amounts of bromine, additional scrubbing system would have to be installed.

Emissions and Secondary Environmental Impact--

The following discussion highlights the possibility of bromine emissions. In addition, products of incomplete combustion (PIC's) are a definite possibility, and these may be more toxic than the original waste.

The possibility of PIC emissions is a serious concern with respect to combustion of hazardous waste fuels in cement kilns because ring formation in the chamber can cause the raw feed to cascade towards the torch under avalanche-like conditions. This cascade pushes the gases before it quenches the flame and thus causes a localized increase in pressure. Reportedly, the flame loss will generate PIC's and the pressure rise will cause the PIC's to discharge through the seals at the torch end of the kiln.

The hazardous effects of bromine emissions were discussed in detail under the incineration option. The secondary environmental impacts of the potentially dangerous PIC emissions are not known, as published test reports contain no substantive information regarding PIC emissions from a kiln. Based on the high POHC destruction efficiencies indicated in these same reports, however, emissions are believed to be insignificant (PEI 1987).

Another aspect of toxic emissions concerns particulates. Whether the introduction of bromine will increase particulate emissions appears to depend on what effect the compound has on the particle size of the emissions. The brominated compounds are expected to react similarly to chlorinated compounds. The latter form hydrogen chloride (HCl) and chlorine (Cl_2) as the chlorinated compounds are oxidized in the combustion process. These, in turn, react with the alkali components in the cement feed to form volatile alkali chlorides such as potassium chloride (KCl) and sodium chloride (NaCl), which condense into a fine fume. Chlorine also promotes a buildup of material on the wall of the kiln that forms a restrictive ring inside the kiln as it rotates. This phenomenon ("ring") restricts the cross-sectional area, which increases the combustion gas velocity and causes more clinker dust to

be carried through the exhaust system. Notwithstanding this scenario, tests have shown that no correlation exists between particulate emissions and the chlorine content of the waste fuel (see Figure 4-2, PEI 1987). Because bromine is less volatile than chlorine, the kiln's dust collection system should adequately abate emissions.

Compatibility--

The process is compatible with the pesticide formulations.

Process Safety and Health Hazards--

Cement kilns have been operating for a long time without any major safety problems. Thus, the basic process is believed to be inherently safe. The possibility of an explosion or fire is also minimal. On the other hand, safety and health hazards could arise from toxic emissions, such as health hazards due to bromine emissions, which were discussed in the section on incineration. Products of incomplete combustion are also regarded as a high health risk and carcinogenic.

Transportation Access to Facility--

The LaFarge facility has railroad access, and the same is believed to be true of the Dundee facility.

Storage and Handling --

Another aspect of plant safety and toxic emissions concerns the handling and storage of the hazardous waste. The possibility of spillage and emissions is at a maximum during the handling and storage of the waste. Most of the constituents of the waste under consideration (EDB, EDC, chloropicrin, etc.) are extremely hazardous and warrant the use of special precautions in

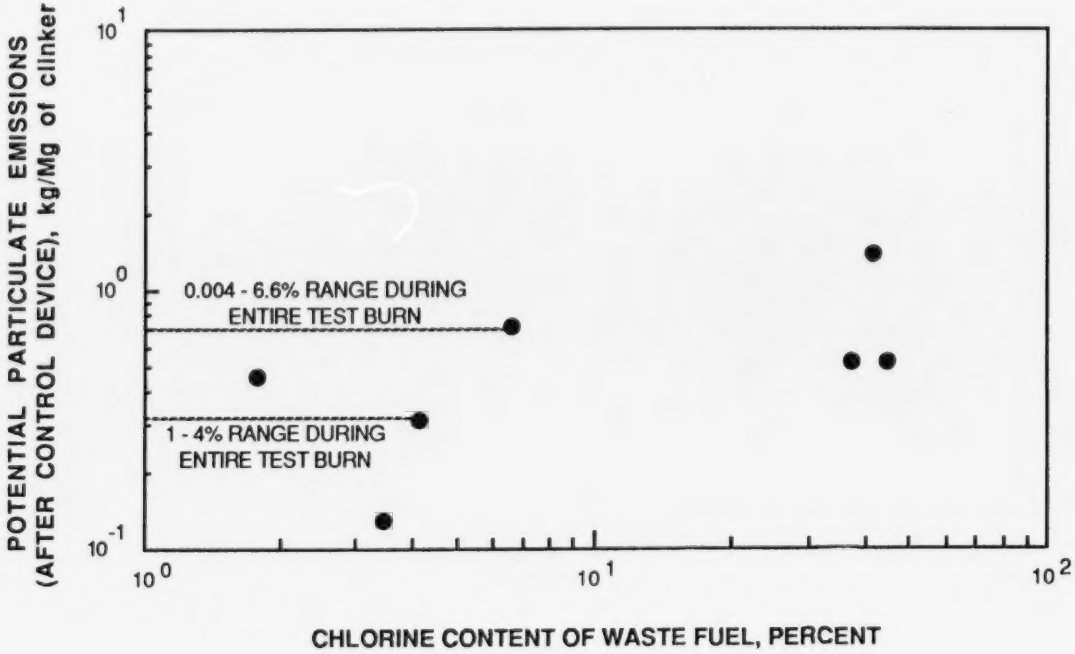


Figure 4-2. Particulate emissions correlated to chlorine content of waste fuels. (PEI, 1987).

their handling. As part of an incineration program, a comprehensive spillage-control action plan should be prepared and all operators should be trained to implement it. The overall layout and design of this area must conform with the standards suggested for hazardous wastes (Bonner et al. 1981). Whether the current design features of cement plants conform is not known. If not, the plants would be more vulnerable in case of accidental spillage.

Preprocessing--

The liquid pesticides must be blended with other liquid fuels in proper ratio to ensure the correct bromine content, as too much bromine could cause emission problems. During the blending of the different liquids, care should be exercised to ensure that the mixture components are compatible. Blending of wastes is relatively routine and requires no additional work or equipment.

Corrosion and Mechanical Reliability--

Bromine and HBr are both very corrosive to most metals. No data are currently available on the extent of corrosion due to bromine and HBr under the conditions prevailing in a cement kiln. Because of the high alkaline environment in the kiln, however, corrosion should not be a serious problem. Therefore, it is believed that the existing material of construction should be able to withstand any corrosive attack due to bromine and HBr. The kiln refractory lining would have to be of high quality and corrosion-resistant. The exhaust gas processing unit may have to be refractory or FRP- or Teflon-lined, depending on the operating temperatures.

Handling and Disposal of Process Residues--

Cement kiln dust is not a hazardous waste, and it is currently exempt from the requirements of RCRA. If brominated compounds were burned in a cement kiln, the content of bromide salts in the residue would increase; however, this would not raise the toxicity of the dust, nor would it be likely to cause a significant increase in the amount of cement dust that is "wasted" (as a result of the fineness of the salt fumes). As with chlorinated compounds, the major portion of the bromine is expected to end up in the clinker as product.

Cost--

The cost figures quoted range from approximately $0.76 to $1.3/lb.

Permitting--

La Farge has an RCRA permit but would require modification, whereas the Dundee facility will need a permit.

Probability of Success--

From a theoretical point of view, the cement kiln option seems to hold a good potential for success. However, trial burns will be required to demonstrate the capabilities, and to establish the optimal feed rates.

Time Schedule--

The optimal feed rate will decide the overall time period to destroy all the pesticide formulations. Assuming that acceptable feed rates are possible, this option should take about a year and a half to complete the operation.

CHEMICAL DESTRUCTION

This option entails two approaches to destroy the EDB formulations. The first approach involves distillation of some of the formulations (CS_2 containing and chloropicrin containing) to recover individual components followed by the destruction of EDB recovered with one of the chemical processes. The other approach involves destruction of the pesticide formulations without any pre-processing. Recent bench-scale testing at the R&D facility of Internation Technology (IT) indicates that the distillation of the CS_2 containing formulations is very easy. The components recovered are quite pure and could be sold for market value. However, distillation of the chloropicrin formulation was found to be difficult because of an azeotrope formation. Also, IT has learned from industry sources that the distillation of chloropicrin can be very dangerous, and hence, this option was not pursued. The feasibility of distilling the miscellaneous formulations was not investigated.

The engineering evaluation of the chemical processes is discussed in the subsequent discussion. This evaluation is based on the test work results, preliminary process calculations and cost estimates.

Zinc Process

Status and Accessibility--

The zinc (Zn) process is still in the conceptual stage. Recent laboratory tests on pesticide formulations have given mixed results as regards the EDB destruction efficiencies; however, extensive pilot-scale testing would be required to demonstrate process feasibility, performance capabilities (DREs), process economics, and commercial reliability.

Past Experience--

No one has had previous experience with a full-scale zinc process. The following important observations were made during recent bench scale testing of the zinc process with carbon disulfide containing and chloropicrin containing formulations at IT:

* Destruction of pure EDB (obtained by distillation of carbon disulfide containing formulations) was 99.93 percent complete, requiring very little (0.008 gms of HCl/gm of EDB) acid. However, the above result was obtained after keeping the reactants in contact for 42 hours with 10.5 hours of total agitation time.

* For the chloropicrin formulations, destruction of EDB was about 90 percent while that of chloropicrin was about 93 percent. The products of chloropicrin reaction could not be identified (Test results indicate formation of some unknown compounds). Acid consumption was 0.46 gms of HCl/gm of pesticide, while the zinc consumption was 0.74 gms of zinc per gram of pesticide (about 5 times the theoretical requirement). Also, it has been reported that the reaction proceeds very slowly since the zinc particles get coated with the reaction products. The zinc particles had to be replaced once during the reaction to improve the reaction rate and efficiency. Intense agitation and a pH of less than 1 were required to keep the zinc surface clean of any coating due to the reaction products. The overall agitation time for this reaction was about 23.5 hours (the reaction mixture was studied for more than 5 days). The reactor effluent gas was found to contain ethylene and hydrogen.

* For the carbon disulfide containing formulations the EDB destruction was about 23 percent after 11 hours of agitation. This poor destruction may be attributed to the fact that carbon disulfide seems to react with the zinc producing some sulfide compounds (carbon disulfide destruction was 81 percent and both the liquid and gas phases had sulfide odor). Also, carbon tetrachloride was found to react with the zinc (31 percent conversion). However, the reaction products have not been identified. The acid consumption was approximately 0.34 gms/gm of pesticide. The gaseous reaction products were ethylene and some amount of hydrogen.

In addition to the above, it is now known that the zinc dehalogenation reactions are highly exothermic, creating a problem of heat removal (Appendix A). It is also clear that the CS_2 containing formulations would have to be distilled prior to treatment by the zinc process.

Need for Development--

The need for further development of the zinc process cannot be overemphasized. An extensive test program would need to be undertaken to establish the engineering feasibility and DREs attainable, to collect process design data, and to determine potential problem areas. Some of the areas that should be researched during the test runs include:

1) The zinc process does not seem to give the 4 nines destruction efficiency with the chloropicrin formulation. More tests would be needed to establish if 4 nine DREs are attainable, or to study the feasibility of distilling the chloropicrin formulations. The test results seem to indicate that the presence of other constituents hinder the EDB reaction giving lower DRES. Thus, more tests would be required to establish the DREs attainable with the miscellaneous formulations.

2) The test results seem to indicate very long reaction times for achieving maximum destruction. However, the test work does not provide any kinetic data to establish reaction rates. The zinc dehalogenation reaction is highly exothermic which could lead to problems of heat removal. Depending upon the relative rates of the reaction and heat transfer, the overall process rate would be controlled by either the reaction kinetics or the heat transfer. If reaction rate is much faster than the rate of heat transfer (rate of reaction >> rate of heat removal), then the overall rate would be controlled by the rate of heat transfer (an assumption in the process calculations - Appendix A). On the other hand,if the reaction rate is much lower than the rate of heat transfer (rate of reaction << rate of heat transfer), then the overall rate would be governed by the reaction kinetics. As can be seen from the above, it is important to establish the controlling mechanism, as it will affect the process design, time of operation, and hence, the overall process economics.

3) Preliminary test results indicate high zinc and acid consumptions (especially for the chloropicrin formulations). However, it is believed that the problem of zinc coating can be solved without using excess acid. The cost estimates for this process were developed assuming very minimal acid requirements. However, the problem of zinc coating and acid requirement would have to be studied in more detail in subsequent tests. If the acid requirements are high, expensive material of construction would be required to withstand the corrosion. The use of common polymeric materials of construction may be difficult because of the heat transfer requirements of

the system and because most common synthetic materials are not recommended for halogenated hydrocarbons (Mellan, 1976). One suggestion made during the senior technical review involves slurrying the zinc with water in the reactor after which the pesticide and the concentrated acid would be added at a metered rate. The feasibility of this, and any other option would have to be studied by conducting pilot-scale testing.

4) The extent to which Zn reacts with other constituents of the pesticide formulations [carbon tetrachloride (CCl_4), chloroform, ethylene dichloride (EDC), sulfur dioxide (SO_2), carbon disulfide (CS_2), etc.] and the products of these reactions should be determined. Test results indicate formation of unknown products. All unknown products would have to be identified to decide if the effluents are hazardous or otherwise. These data will be valuable in deciding the ultimate disposal methods for the reactor effluents and in estimating the reagent requirements. Both the factors have a significant impact on the operating costs.

5) The feasibility of recovering byproducts of value from the reactor effluent stream needs to be studied. Thus, the reactor effluent must be characterized and a process design must be developed to accomplish this task.

Other Areas of Concern--

Equilibrium calculations for the initial reaction mixture show that the mixture would boil between 60° and 70°C. Therefore, using a vacuum pump to remove the ethylene could result in a significant loss of organics into the vapor phase. It would be difficult to condense these organics under sub-atmospheric pressures using an overhead condenser. This creates a possibility of emissions problems. Moreover, with vacuum in the system, there is a possibility of air leaking into the system due to some malfunction. The mixture of air and the gases in the system (ethylene, and other organic vapors) could create an explosion hazard. Thus, it is felt that this aspect should be studied in future tests with this process. The reaction gases could be removed from the system by flowing an inert gas (like nitrogen) or by putting a fan between the reactor and condenser. The former was assumed for the preliminary cost estimates. Using an inert gas will reduce the partial pressures of the pesticide constituents in the vapor phase which will reduce the volatility, and hence, loss of organics.

Need for Additional Equipment or New Equipment--

Two options were available for the zinc process to destroy pesticide formulations. The first involved the construction of a new facility; the

second entailed the use of some existing equipment from the GARD facility in combination with new equipment. Reactor vessels, a filter press, and a flare and stack are available at the GARD facility; the remainder of the equipment will have to be new. If further tests determine high acid requirements, however, the GARD option will become infeasible because of corrosion concerns. The need to construct a new facility would affect the time required to complete the overall project.

Toxic Emissions and Secondary Environmental Impact--

Currently, the only possible emissions from the process operation appear to be due to volatile organics escaping the reaction system and ethylene gas. The secondary environmental impact due to volatile organics from pesticide formulations needs to be studied in detail. Ethylene is reported to be herbicidal and is known to affect vegetation. The other probable source of emissions would be the handling of the pesticide itself.

Compatibility--

Bench scale tests show that the CS_2 in the formulations reacts vigorously with the zinc, thereby retarding the rate of EDB reaction. Thus, CS_2 would have to be removed by distillation prior to treatment of the pesticide formulation by zinc process.

Safety and Health Hazards--

One of the major products of the process is ethylene gas. Because ethylene is highly flammable, the probability of a fire hazard would be high. In addition, the reactor off gases may contain some volatile organics which increase the explosion and fire risks. Thus, process safety should be a

primary concern. Ethylene, however, is not as dangerous to handle as is acetylene; in fact, its handling is routine in the petrochemical industry. If proper care is exercised, the probability of a major accident could be minimized. If further studies indicate high acid requirements to keep the zinc surface active for reaction, then hydrogen may also be formed by the reaction between Zn and HCl. This would create additional safety concerns.

Most of the constituents of the formulations are very harmful; therefore, the operators who handle these wastes would have to wear special clothing. Should a fire occur, toxic emissions from the burning of these formulations are also a possibility.

Transportation Access to the Facility--

This access would have to be provided during construction.

Storage and Handling of Waste--

Another aspect of plant safety and toxic emissions concerns the handling and storage of the hazardous waste. Most of the constituents of the waste under consideration (e.g., EDB, EDC, chloropicrin), are extremely hazardous and warrant special precaution during handling. Before undertaking a chemical destruction program, a comprehensive spillage control action plan should be prepared, and all operators should be trained to implement it. Because several commercial facilities handle hazardous waste regularly, designing this area of the plant should be fairly routine.

Corrosion and Mechanical Reliability--

It is believed that the problem of zinc coating can be solved without consuming large quantities of HCl (e.g., using intense agitation). If this

belief could be validated during further testing, then corrosion should not be a major concern. However, if substantial amount of hydrochloric acid (HCl) is required in the reactor to clean the surface of zinc particles, then corrosion would be an important consideration, necessitating the use of expensive materials of construction.

High-powered mixers would be required to keep the zinc particles in the reactor mixture in suspension. The extent of erosion-corrosion due to the zinc (if any) may need to be researched; however, it is not expected to pose a major problem.

Handling and Disposal of Process Residues--

Test work would have to establish if the process effluents are hazardous or nonhazardous. Depending on the nature of the effluents, appropriate disposal methods would have to be adopted. These can have a significant impact on the total cost.

The process generates a large quantity of effluents. Disposal of these effluents has a significant impact on the overall process economics. Although pure zinc bromide and chloride have a good market value, it is not known if there will be any demand for these compounds obtained as the by-products of a hazardous waste treatment. The feasibility of recovering byproducts of value would have to be established on the basis of test work. Zinc bromide solution has applications in enhanced oil recovery. It is not known if the aqueous effluents from the process could be shipped to an enhanced oil recovery facility for value. Hence, for this analysis the worst case is assumed where the effluents have to be disposed of as hazardous

wastes. Since the organic and aqueous phases are immiscible, they can be easily separated in a phase separator. It is assumed that the organic phase is destroyed by incineration at 50 cents/pound. Inquiries with industry sources indicated that the aqueous waste could be disposed by deep well injection or in a landfill or a wastewater treatment facility. The disposal costs quoted varied from 12 cents/gallon for deepwell injection to about 90 cents/gallon for waste stabilization and disposal. Thus, a disposal cost of 50 cents/gallon has been assumed. However, if the actual costs differ substantially from the above estimates, the overall cost would change substantially.

Cost--

Preliminary study cost estimates have been developed for this process (Appendix B) based on approximate process calculations (Appendix A) to size the equipment and estimate reagent consumption. It has been assumed that the CS_2 formulations are distilled prior to destruction. The recovered products (CCl_4 and CS_2) are sold at market value. The cost of recovering reaction byproducts was excluded because of lack of sufficient data. Instead, the worst case of effluent disposal as a hazardous waste has been assumed.

The primary cost estimates have been developed assuming that the problem of zinc coating is solved without using excess HCl. Two economic options have been considered: a) build a new facility, and b) use some equipment at the GARD facility. Cost estimates have been developed for two situations: 1) the government owns and operates the facility, and 2) the work is subcontracted to a small scale chemical firm. Subcontracting the destruction to

another company is not applicable to the option of utilizing the GARD equipment. Under the first option the entire fixed capital cost is included under the carrying charges, while under the second option the depreciation charges are included under the carrying charges. The depreciation charge has been estimated assuming straight line depreciation, 10 year life span and zero salvage value. The unitized cost for treating all the formulations, under each operating option is:

New facility

Government owns and operates the facility:	$0.50/lb
Subcontracted to small chemical firm:	$0.3/lb

Option of utilizing GARD equipment

Government owns and operates facility:	$0.44/lb

The above estimates do not include the costs for permitting and land lease. Also, since this process option would require much more testing prior to ultimate disposal, the cost of storing these formulations and the development costs should also be added to the above costs. Further, these estimates have been developed assuming an efficient operation (no outage), and two trains of equipment operating per shift. Two equipment trains were assumed because of the urgency to dispose of these formulations as quickly as possible. The above costs change very slightly if single train operation is assumed.

It is evident from the earlier discussion that a number of factors affecting the process have not been established. These factors (overall reaction time, reagent requirements, effluent disposal, etc.) can have a substantial impact on the costs estimates.

Permitting--

Permits to handle and destroy the pesticide formulations would be required under each of the options.

Probability of Success--

The preceding discussion points to a need for more test work to establish the feasibility of this process. The process seems to perform very well with pure EDB. However, the presence of other constituents seem to affect the process performance. Very long overall reaction times are needed to achieve 99.99 percent destruction. Thus, although the process seems to have a good promise, much more extensive testing would be required prior to a final judgement.

Time Schedule--

In view of the uncertainities associated with this process, extensive testing would be required prior to scale-up. This would increase the overall time required to dispose the pesticide formulations. Assuming that adequate reaction rates are achievable, the overall disposal time could be about 2.5 years.

ATEG Process

Status and Accessibility--

The ATEG process is still in the conceptual stage. The EPA has demonstrated its capabilities to achieve the required levels of destruction on a laboratory scale, and the results of these tests have encouraged further testing. The technology would become available, however, only after pilot-scale testing to demonstrate its feasibility, performance capabilities (DREs),

process economics, and commercial reliability. The process and operational data derived from such testing will be important to the completion of a detailed process engineering design.

Past Experience--

Because the process is still in the conceptual stage, no one has had previous experience with commercial operation. The current data base is limited to lab scale tests conducted or sponsored by the EPA/GARD and recent bench scale testing by International Technology (IT). The results of the tests carried out by the EPA have already been reported in Section 3. The results of IT's test-work are summarized below:

- Destruction of EDB bottoms from the distillation of carbon disulfide containing formulations was about 100 percent complete. However, the reaction seems to be very sensitive to the amount of TEG and the concentration of caustic solution used in the system. During large scale reactions it was observed that the reaction temperature had to be greater than 35 °C for the reaction to occur. Also, a reaction inception time of about 30 minutes was observed. However, there are no data available on the reaction rates.

- The reaction of ATEG with chloropicrin formulations was studied on a small scale (10 to 50 mls samples). The reaction was studied using relatively high amounts of TEG, and with two different caustic solutions. With a 30 percent caustic solution, the destruction of EDB was complete. However, none of the chloropicrin seems to have reacted. This is an important observation as it creates a possibility of treating the chloropicrin formulation with the ATEG. No further tests were carried out for the chloropicrin formulation.

- Treatment of carbon disulfide containing formulations with the ATEG process resulted in high TEG consumptions to achieve EDB destruction, while at low TEG concentrations there was almost no EDB destruction. This is because of the reaction of carbon disulfide with the TEG. The overall reaction time for the carbon disulfide formulations was more than 8 hours.

- The reaction of vinyl bromide with the KTEG solution was studied to a limited extent. It has been reported that a gel-like layer was formed on top of the KTEG solution in which the vinyl bromide became trapped. This layer was found to be water soluble and released acetylene upon dissolution.

Need for Development--

The preceding discussion points up an obvious need for further development of this process. Although patented by EPA, the process would require comprehensive testing on a pilot scale to establish its process feasibility, to collect valuable process design and operating data, and to ascertain potential problem areas. Some of the questions that need to be addressed during the test work are:

1) It is believed that the reaction of chloropicrin with ATEG forms a number of chlorinated by-products which may be hazardous. However, IT test results seem to indicate that it may be possible to selectively treat the EDB in chloropicrin formulations by using a 30 percent caustic solution. In the absence of any positive data, treatment of chloropicrin formulations with the ATEG process is still an open-ended question. More tests would be required to test the feasibility of treating these formulations as is, or to study alternative methods of distilling the formulations (e.g., azeotropic distillations etc.). If the ATEG process cannot treat the chloropicrin formulations, then it would not be a very attractive option. As regards the miscellaneous formulation (which form the largest percentage of the total EDB formulations to be destroyed), more tests would be needed to establish the DREs.

2) The bench scale test data has not established the overall reaction time to achieve acceptable DRE (99.99). Establishing the reaction time is very important as it has a direct impact on the overall time required to destroy all the pesticide formulations. The overall operating cost (labor) is directly proportional to this time. If the overall processing time is larger than that assumed in the preliminary study estimates (Appendix A and B), then the overall cost for this process will be much higher than those indicated.

3) How much reaction other constituents (carbon tetrachloride, chloroform, methyl chloride) undergo and the analysis of the products (gas, liquid, or solid) should be determined more thoroughly. This will have a direct bearing on the design of downstream processing units. Also, analysis of the reaction effluents is important with regard to their ultimate disposal, which can significantly affect the process costs.

4) The feasibility of the proposed feeding of solid NaOH (which is hygroscopic and absorbs moisture) to the reactor should be reviewed. Hydrated NaOH could be difficult to transport. Controlled feeding of NaOH must be followed to avoid any runaway reactions.

5) Vinyl bromide and vinyl chloride are both carcinogenic compounds. The efficient removal of these and any other gaseous products of the reaction and, hence, the quantification of the scrubber performance are very important. The EPA has proposed a countercurrent packed-bed (regular packings) tower. Vinyl halides react with KTEG to form acetylene gas and potassium salts. The following operational data need to be established from the testing program:

   a) The extent of vinyl halide removal.

   b) Test results seem to indicate that the dehydrohalogenation of vinyl bromide using KTEG forms a gummy layer which dissolves in water with the evolution of acetylene. This raises questions about the choice of the scrubber. The KTEG solution by itself is very viscous, and with "gummy mass" being formed, it can clog the scrubber. This can lead to serious operating problems (pressure buildup in the system, incomplete absorption of vinyl halides etc.).

   c) More tests should be undertaken to determine if aqueous KOH solution with very small amount of TEG (similar to the reactor) could be used in the scrubber to eliminate the vinyl halides. If possible, this scheme will reduce the reagent consumptions, eliminate the need to recirculate the scrubber effluent liquid and eliminate problems of clogging etc. If not, the scrubber will pose serious operational and safety concerns. A possible alternative to handle the gas scrubbing would be to use a batch operated agitated contactor or bubble column. Agitated contactors and bubble columns both give very high mass and heat transfer characterisitcs and are ideal for handling systems forming solids or which are viscous. Also, operating the contactor in a batch mode would help in reducing the reagent consumption. However, in order to ensure complete destruction of the vinyl halides the effluent gas may have to be recirculated. This would involve recompressing the off gases which could be dangerous with acetylene being formed in the system.

6) The solids content of the reactor liquid effluents should be ascertained during the test work, along with the type of solid-liquid separation operation required to remove them. The EPA wants to recover reaction byproducts with some resale value. The technical feasibility and the probable flow sheet for such an operation should be researched.

Other Items of Concern--

1) EPA has suggested the use of a vacuum pump to remove the acetylene from the system. However, as discussed under the zinc process,

maintaining vacuum could lead to a loss of organics. Like the zinc process, it is felt that this aspect should be studied during future tests, although it would be safer to use inert gas or a fan to remove reactor gases.

2) Process calculations show that using solid NaOH in the system creates a situation where the percentage solids in the reactor exceeds 30 percent. Higher percentage of solids would make mixing and heat transfer very difficult, and the slurry may not be pumpable. As a result water may have to be added to the system to keep the percentage solids lower than 20 percent. Thus, instead of feeding solid NaOH flakes, it is felt that an alkali solution should be used in the reactor. This will eliminate the problem of feeding solid alkali to the reactor while eliminating problems of higher percentage solids in the reactor and poor heat transfer.

3) Introduction of an inert gas in the reactor (to purge process gases) would reduce the partial pressure of the vinyl halides in the scrubber section, reducing the driving force for their dissolution in the liquid phase. Vinyl halides are very stable compounds and it is difficult to dehydrohalogenate them (Morrison and Boyd, 1973). Thus, detailed pilot scale testing of the scrubber operation is imperative to assure complete neutralization of vinyl halides in order to avoid problems of toxic emissions.

Need for Additional or New Equipment--

Two options (process variations) are available for the chemical destruction of pesticides via ATEG. Under the first option, EPA would build a totally new facility; under the second option, some existing equipment from the GARD facility would be used in combination with other new equipment. The only equipment reportedly available at the GARD facility are reactors, a filter press, a flare, and a stack. The rest of the equipment would have to be new. (The cost data for both options are presented in Appendix B.) The need to construct a new facility (under both options) would affect the time period required for completing the overall project.

Toxic Emissions and Secondary Environmental Impact--

Vinyl chloride and vinyl bromide emissions could be generated. Both compounds are carcinogenic. In addition, both chemicals are highly flammable

and produce toxic gases on ignition. Because the scrubber tower discharge gases are burned before their release to the atmosphere, this potential source of toxic emissions can create a secondary environmental impact. In addition, toxic emissions due some of the volatile organics escaping the system are possible. The possibility of toxic emissions due to the reaction of ATEG with other constituents of the formulations needs to be researched.

Compatibility--

CS_2 is not compatible with TEG, producing a gummy mixture and restricting process operation.

Safety and Health Hazards--

The products of the reaction (i.e., vinyl chloride, vinyl bromide, and acetylene) are all highly flammable; acetylene is also very explosive. In addition, the effluent gases may contain volatile organics from the reaction system, creating safety and health hazards. Thus, the fire and explosion risks associated with the ATEG process must be considered. Process safety will be a primary concern. Moreover, because the reactions involved are highly exothermic and rapid, runaway reactions are a possibility. Such an event could precipitate the danger of these product gases catching fire and causing an explosion. Therefore, great care must be exercised in its operation. An operating option that would probably reduce these risks entails feeding the pesticide to the caustic solution at a controlled rate, with a temperature control to cut off the feed. As indicated previously, all options would need testing prior to scaleup.

As mentioned earlier, vinyl chloride and vinyl bromide are carcinogenic. Exposures in high concentrations can cause dizziness, anesthesia, and lung

irritation. Irritation of eyes, nose, and throat is also common. Chronic exposures to vinyl chloride can cause liver damage. Both chemicals are highly flammable, and when ignited, they emit toxic gases that can create health hazards.

Most of the constituents of the pesticide formulations are harmful, and operators should wear special clothing when handling these wastes.

Transportation Access to Facility--

This access would have to be provided during design and construction.

Storage and Handling of Waste--

Another aspect of plant safety and toxic emissions is the handling and storage of the hazardous waste. Most of the constituents of the waste under consideration (i.e., EDB, EDC, chloropicrin, etc.) are extremely hazardous and warrant special precaution in handling. Before a chemical destruction program is undertaken, a comprehensive spillage control action plan should be prepared and all operators should be trained to implement it. Several commercial facilities handle hazardous waste regularly; thus, designing this area of the plant should be fairly routine.

Corrosion and Mechanical Reliability--

The corrosivity of vinyl chloride, bromide, NaOH, and alkali salts is unknown; however, 316 stainless steel should be a suitable material of construction for the key equipment items to avoid extensive corrosion. However, more data would be needed establish suitability of SS316.

The explosive characteristic of the reaction products should be considered during the mechanical design of the process equipment. On the whole, the construction should have good mechanical reliability.

Handling and Disposal of Process Residues--

The disposal of process effluents is an important factor in the overall process cost. Test work would have to establish if the process effluents can be classified as hazardous or nonhazardous waste. Depending on the nature of effluents, appropriate disposal methods would have to be adopted, which can have a significant impact on total cost. The feasibility of recovering byproducts of value would have to be established on the basis of test work results. In the mean time, for this evaluation the worst case of effluent disposal as a hazardous waste has been assumed for cost purposes. As in the case of zinc process, it is assumed that the organic and aqueous effluents from the reactor are completely immiscible, and hence, are easily separated in a phase separator. The organic phase is assumed to be disposed by incineration while the aqueous layer is assumed to be disposed suitably.

Cost--

Preliminary study cost estimates have been developed for this process (Appendix B) based on approximate process calculations (Appendix A) to size the equipment and estimate reagent consumption. It has been assumed that the CS_2 formulations are distilled prior to destruction. The recovered products (CCl_4 and CS_2) are sold at market value. The cost for destroying chloropicrin formulations has not been included because of the high uncertainty associated with it. The chloropicrin stock may be assumed to be destroyed by some other process at the same unitized cost as that obtained for the other formulations. The cost of recovering reaction byproducts was excluded because of a lack of sufficient data. Instead, the worst case of effluent disposal as a hazardous waste has been assumed.

There are two options for this process:

1) Government owns and operates the facility.
2) Contract to small-scale chemical firm.

Under the first option, the government could either build a totally new facility or utilize some process equipment available at the GARD facility. Under the second option, the capital cost is calculated assuming a new facility; however, this cost is depreciated using a straight-line depreciation method and assuming a 10-year life and zero salvage value.

The unitized cost are:

	Government owns and operates	Subcontracted to small firm
New facility	$0.78/lb	$0.34/lb
GARD option	$0.71/lb	

The above estimates do not include the costs for permitting and land lease. Also, since this process option would require much more testing prior to ultimate disposal, the cost of storing these formulations and development costs should also be included to the above costs. Further, these estimates have been developed assuming an efficient operation (no outage) and two trains of equipment operating per shift. Two equipment trains were assumed because of the urgency to dispose of these formulations as quickly as possible. The above costs change very slightly if single train operation is assumed.

It is evident from the earlier discussion that a number of factors affecting the process have not been established. These factors (overall reaction time, reagent requirements, effluent disposal, etc.) can have a substantial impact on the cost estimates.

Permitting--

Permits to handle and destroy the pesticides would be required under each option.

Probability of Success--

The ATEG process seems to demonstrate the necessary capability to destroy EDB. Preliminary test results seem to indicate that it has the capability to selectively eliminate the EDB in the chloropicrin formulations, eliminating the need for preprocessing and the problem of forming unknown by-products. However, this aspect would have to be thoroughly researched.

Although the process seems capable, it is complicated by a two stage reaction involving a number of reactants (NaOH, KOH, TEG) and forms a wide spectrum of by-products which could make characterization and ultimate disposal difficult. Moreover, the process poses safety concerns as it involves the handling of acetylene. Bench-scale tests show that the process is sensitive to a number of operating parameters (TEG concentration, NaOH concentration, reaction temperature, etc.) requiring further testing to ascertain the optimal process conditions. Further tests would also be required to establish the process chemistry, the reaction kinetics and operating procedures.

Time Schedule--

In view of the extensive testing that would be required prior to ultimate disposal, it is believed that this option could take about two and half years.

SECTION 5

CONCLUSIONS AND RECOMMENDATIONS

SUMMARY

In this study, all available alternatives have been considered that have potential for the successful destruction of EDB formulations within the next 2 years. To facilitate a comparison of the alternatives on an equal basis, selection criteria were developed that covered all major technical issues as well as the overall cost. This permitted a direct comparison of the technical competence of the various alternatives. Such a comparison pointed up the technical merits and shortcomings as well as the areas of uncertainty for each alternative. Based on all information available to date, it appears that incineration in the presence of sulfur dioxide is the best alternative for effective, rapid, and economical destruction of all the EDB stocks.

Preliminary design and cost estimates were made for each of the chemical destruction processes; however, these calculations were made on the basis of very limited laboratory-scale test data and included several engineering assumptions (Appendix A). Some of these assumptions may not hold in actual operation, and the costs could be affected. Also, the cost figures reported are exclusive of such important cost items as permitting, land lease, interim storage, etc. These costs will have to be incorporated in the reported cost figures to arrive at the overall cost of destroying the pesticide formulations.

The costs for the thermal destruction options were obtained from vendors and represent an average incineration cost. Cost figures for specific

modifications (e.g., starved-air incineration and incineration in the presence of sulfur dioxide) could not be obtained from vendors; however, EPA has received proposals from Rollins Environmental and the John Zink Company for these processes. Rollins has proposed using the sulfur dioxide technology, whereas John Zink has suggested starved-air incineration. Thus, the EPA should be in a position to establish the cost-effectiveness of each option.

CONCLUSIONS

From a technical standpoint, both starved-air incineration and destruction in an existing incineration facility without any modifications appear to be infeasible because of the bromine emissions that would exit through the stack.

Incineration in the presence of sulfur-containing waste holds an excellent promise for the elimination of bromine emissions. The test burn results (Alliance, 1988) show that this option meets the destruction standards for POHCs (DREs greater than 99.9999 percent) and emission standards (bromine below detection limits and bromide about 20 µg/dscf in the stack). Also, continuous monitoring data for CO_2, O_2, CO, NO_x, and SO_2 seem to be well within the established standards. Bromine mass balance indicates that all the bromine exits the system in the scrubber water. Also, the fact that a currently operating incineration facility in Europe is successfully using this technology to destroy halogenated waste lends credibility to this option (Fabian et al., 1979). Moreover, this option offers the advantage of speedy disposal of the entire EDB stock (probably less than a year) at a competitive cost. This is especially important in view of the urgency of the situation. Thus, incineration in the presence of sulfur dioxide appears to be the best choice for destroying the EDB pesticides.

Cement kiln incineration appears to be a promising option; however, extensive testing would be required to establish the performance capabilities and optimal waste feed rates. The optimal waste feed rate would have to be determined so as to eliminate bromine emissions in the flue gases while not having an adverse effect on product quality. If the allowable feed rate was low, the overall time to complete the job would be higher. This, in turn, could increase the overall cost of this option; however, no definitive estimates can be made until after test burns are performed.

The ATEG process has shown excellent capability to eliminate the EDB obtained from the distillation of the CS_2 formulations. Previously the treatment of chloropicrin formulations with the ATEG process was regarded infeasible because of fear of forming unknown, and perhaps more hazardous compounds. However, preliminary tests seem to suggest that it may be possible to treat these formulations, without reacting the chloropicrin, by using a 30 percent caustic solution. This approach, however, needs further testing to prove its validity. The bench-scale tests seem to indicate that the presence of other constituents in the pesticide formulations interfere with the EDB destruction. Thus, extensive tests would also be required to study the feasibility of treating the miscellaneous formulations, without preprocessing them. Despite the promising results on the laboratory scale, the ATEG process could create operational problems because of its compexity. The process involves:

- A two step reaction.
- Number of reactants (NaOH, KOH, TEG).
- It is found to be sensitive to a number of operating parameters like the TEG concentration, caustic concentration, temperature, etc.

- Handling of potentially hazardous substances like vinyl bromide, etc.

- The process forms a wide range of byproducts, which could make disposal of the effluents difficult.

It is therefore evident that the process would need very extensive testing to eliminate uncertainties and operational difficulties and establish the optimal operating conditions, prior to design and scale-up. This could take considerable time, causing a delay in the overall disposal of the EDB pesticides.

Bench-scale tests with the zinc process show excellent promise with pure EDB. Disposal of the chloropicrin formulations seems to be a problem because of unacceptable levels of DREs, formation of unknown products, high zinc consumption, and high hydrochloric acid consumption. Reaction of zinc with the CS_2 formulations show that the carbon disulfide reacts rapidly with the zinc, resulting in very poor destruction of EDB. In all the tests with the zinc process, long reaction times were required to achieve substantial EDB destruction. Even longer reaction times may be required to achieve 99.99 percent destructions. This could potentially make the process infeasible. Therefore, more tests would be required to determine:

- Ways to achieve 99.99 percent destruction with all formulations, without any preprocessing. CS_2 may have to be removed prior to treatment.

- Ways to reduce the acid and zinc consumption, especially with the chloropicrin formulation.

- Feasibility of an azeotropic distillation of chloropicrin formulations using alcohol, as suggested by IT, if the 99.99 percent destruction of the formulation is not possible.

- The overall reaction time. This is an exothermic reaction. Thus, if the reaction rate is fast, then heat transfer will control the overall rate and vice versa. This will affect the process design and cost.

It is therefore evident that this process would need thorough pilot plant testing to establish its feasibility and optimum operating conditions prior to design and scale-up. The process is more complex than previously envisaged.

At this point in time, incineration in the presence of sulfur dioxide seems to be the most viable and rapid way of disposing the pesticide formulations at a cost comparable to or lower than other methods. Successful trial burns for this method have been completed. As a result, the destruction process can be initiated immediately. The overall time for disposal should be less than six months. In view of the urgency for disposing of the pesticides, this process appears to be clearly the best choice.

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APPENDIX A

PROCESS CALCULATIONS

In order to prepare a comparative cost and performance analysis between each of the process options available, preliminary process calculations had to be developed for some of the options. These calculations are presented here.

The chemical process options (zinc and ATEG processes) are currently in the conceptual stages. Preliminary calculations have been made to establish the sizes of the major process equipment and the reagent requirements. These calculations are important for preparing the approximate cost estimates. In the absence of any pilot-scale data, a number of simplifying assumptions have been made in these calculations. Hence, the resulting cost estimates are only approximate. More pilot-scale testing will be required before accurate sizing and cost estimates can be made. Nonetheless, these preliminary calculations aid in giving an insight into possible problem areas and overall costs.

For the thermal destruction options, there is a large data base for the cost and performance capabilities. The preliminary calculations are thus limited to establishing the equilibrium gas composition for the starved-air incineration option.

ZINC PROCESS

The basic principles underlying the zinc process have been described in detail in Section 3, along with a conceptual flow sheet. Preliminary material

balance and sizing calculations are presented in this section. The equipment sizing is done for the worst-case feed. Table A-1 presents the composition and amounts of various formulations that need to be destroyed. For this analysis, the CS_2-free formulation at Liberty represents the worst-case feed. Also, to simplify the system, the following preliminary assumptions have been made:

1. Only EDB and EDC react with zinc. Although laboratory tests show that other constituents also undergo reaction, the amount of other constituents is small and, hence, should not alter the size of equipment significantly. Also, the extent and the chemistry of these reactions is not known, which makes estimation for these reactions very difficult. Thus, other constituents of pesticide formulations are assumed to remain inert in the reactor.

2. The IT test results indicate a fairly high HCl consumption to achieve desired levels of destruction. However, EPA believes that the acid consumption can be reduced to very minimal levels by properly operating the system (high agitation). Thus, for these calculations, it has been assumed that the system does not require a large amount of HCl.

3. The reaction of EDB and EDC is 100 percent complete. Although this may not be the case in actual operation, it is valid for preliminary estimating purposes.

4. The process is a batch operation.

5. The CS_2 containing formulations are distilled to yield pure EDB bottoms which is destroyed by the zinc process.

The heat of reaction for EDC and EDB were calculated from the heat of formation data in Lange, 1985. The heat of reaction was calculated as:

$$\Delta H_R = \text{heat of reaction} = \Sigma(\Delta H_f)_{\text{products}} - \Sigma(\Delta H_f)_{\text{reactants}}$$

thus,

$$(\Delta HR)_{EDC} = 118{,}580 \text{ Btu/lb-mole}$$

$$(\Delta HR)_{EDB} = 113{,}360 \text{ Btu/lb-mole}$$

It is evident from the heat of reaction data that the reactions are highly exothermic. Depending upon the relative rates of reaction and heat

TABLE A-2. COMPOSITION OF EDB STOCKS

"Liberty" Feed Stock

Low-EDB (<2%) With CS_2

Components	Percent of whole
Carbon tetrachloride	80.90
Carbon disulfide	16.00
Sulphur dioxide	1.50
Ethylene dibromide (EDB)	1.20
Pentane	0.40

Approximately 785,245 lb

High-EDB With CS_2

Components	Percent of whole
Carbon tetrachloride	73.32
Carbon disulfide	15.13
Sulphur dioxide	1.17
EDB	5.49
Ethylene dichloride (EDC)	0.06
Chloroform	4.52
Pentane	0.31

Approximately 624,031 lb

Low-EDB Without CS_2

Not applicable - All low EDB formulations have CS_2

High-EDB Without CS_2

EDC	25.69
Carbon tetrachloride	16.46
EDB	49.44
Sulphur dioxide	0.80
Naphtha	4.31
Methyl chloride	1.26
Others	1.98

Approximately 1,505,794 lb

"Ashburn" Feed Stock

Components	Percent of whole
EDB	38.71
Chloropicrin	31.61
Naphtha	29.68

Approximately 865,095 lb

transfer, the overall reaction rate may be limited by the reaction kinetics (rate of reaction << rate of heat transfer), or the rate of heat transfer (heat transfer << reaction rate). Since there are no kinetic data available on these reactions, for the present calculations it has been assumed that the overall rate is controlled by heat transfer; i.e., overall reaction time is limited by the rate of heat removal from the system under the design constraints. Some options for heat removal include:

1. Remove excess heat as steam by pouring excess water into the system. As the heat of vaporization for water is very high, large amounts of heat can be removed. However, in the present situation, this option doesn't seem very attractive. Elementary vapor-liquid equilibrium calculations made for the initial reaction mixture (mixture boiling point calculations) show that in the presence of water, which is immiscible with the organic phase, the mixture will boil between 60° and 70°C. Also, the vapor phase would have a very high percentage of organics, and the overall heat of vaporization of the reaction mixture would be less than about 200 Btu/lb (110 cal/g << 540 cal/g of water). Thus, this option is ruled out.

2. Another option is to remove heat by using an external heat exchanger. Under this option, the reactor contents would be recycled through an external heat exchanger, where some of the heat would be removed. The cooled reaction mixture would be recirculated back into the reactor.

3. Carry out the reaction at a rate where the heat generated can be removed through the reactor cooling system.

Since the reactions are highly exothermic, it will not be possible to achieve high processing rates with Option 3. Thus, a combination of Options 2 and 3 is considered here.

Assuming that 300 gallons of pesticide (density = 13.16 lbs/gal) are treated per batch,

Amount of pesticide treated = 3948 lbs

EDC treated per batch = 1014 lbs = 10.25 lb mole

EDB treated per batch = 1952 lbs = 10.4 lb mole

Thus,

zinc required at 20 percent excess is:

Zinc = (10.25 + 10.4) x 65.38 x 1.2

= 1620 lbs

On the basis of the tests carried out by the EPA, water and some HCl will have to be added to the reactor along with the zinc. Water is added to dissolve the zinc bromide and chloride salts that are formed by the reaction, while the acid is added to clean the zinc surface.

Amount of $ZnCl_2$ formed = 10.25 lb-moles or 1397 lbs/batch

Amount of $ZnBr_2$ formed = 10.4 lb-moles or 2342 lbs/batch

The reactor is assumed to be at 113°F, and at this reaction temperature the solubility of $ZnBr_2$ in water is 447 g/100 cm^3 and the solubility of $ZnCl_2$ in water is 432 g/100 cm^3.

Assuming that the dissolutions of the salts are independent of each other, the amount of water required to dissolve all $ZnCl_2$ is 39 gallons and the amount of water required to dissolve all $ZnBr_2$ is 63 gallons.

Since it is assumed that the solubility of one salt does not affect that of the other, the minimum water requirement to dissolve all salts would be 63 gallons. However, to account for any change in solubilities of the salts, it is assumed that 30 percent excess water is added to the system. Thus, the amount of water that should be added to the batch is 82 gallons.

According to EPA, the HCl required would be 2 drops of 30 percent HCl per 20 ml of water, or 1 ml/20 ml water. Thus, the HCl required per batch is 4.09 (4.1) gallons. Therefore, a reactor with an overall volume of 500 gallons should be adequate to treat 300 gallons of pesticide.

Assuming a reaction time of 3 hours,

Zn feed rate = 1620/(3 x 60) = 9 lb/min

HCl feed pump capacity = 1.4 gph

Pesticide feed pump capacity = 30 gal/min

Heat Effects in Reactor:

Assuming that the reaction proceeds at a uniform rate during the entire reaction time (actually, there could be sudden surges) gives:

$(\Delta H)_R$ = 10.25 x 118,580 x 1/3 + 10.4 x 113,360 x 1/3

= 798,130 Btu/h

As mentioned earlier, it is assumed that the heat of reaction is removed through the reactor jacket and an external heat exchanger. A part of the reactor contents (approximately 100 gal/min) is recycled through an external heat exchanger. Thus, the extent of heat removal from the system is calculated as follows:

Heat removed through the jacket:

The approximate heat transfer area for a 500-gallon reactor is about 80 ft^2 (Richardson, 1984). Assuming the overall heat transfer coefficient, U, to be 75 Btu/h ft^2 °F (Kern, 1950) and the temperature driving force (Δt) to be 40°F, we get

Heat removed through jacket = q_1 = 75 x 80 x 40

= 240,000 Btu/h

Calculation of external heat exchanger area:

Amount of heat that needs to be removed through the external heat exchanger:

= 798,130 - 240,000 Btu/h

= 558,130 Btu/h

Assuming a U of 75 Btu/ft^2 °F h, and a Δt of 40°F, we get

$$\text{Area of the external exchanger} = \frac{558,130}{75 \times 40}$$

$$= 186 \text{ ft}^2$$

Assume external heat exchanger area of 200 ft^2

Thus, it should be possible to operate the reactor without having significant temperature rise in the reactor. Thus, it should be possible to operate the reactor at or below 113°F.

Mixture Boiler Point Calculations

The mixture in the reactor consists of an organic phase and an aqueous phase. As the two phases are immiscible, each will act independently of the other. At the start of the reaction, the mixture would be:

Organic phase:

	Weight, %	Mole Fraction[1]
EDC	25.69	0.37
CCl_4	16.46	0.152
EDB	49.44	0.374
Naphtha	4.31	0.085[2]
SO_2	0.86	0.019
MeCl	1.26	
Others	1.98	

[1] MeCl is very volatile (B.P. = -25°C), and hence, may be lost in the vapor phase at room temperature. Also, since the amount of MeCl and the "other" components is low, they are neglected from mole fraction calculations.

[2] Naphtha is assumed to be 100 percent pentane.

Water phase: Ten percent HCl.

However, as the amount of HCl is very small and vapor pressure of HCl is very negligible (Perry, 1963), the contribution to the vapor phase will be only due to water. Hence, this phase is assumed to behave as pure water. In addition, the organic phase is assumed to be an ideal solution. Although, in reality the organic phase will not form an ideal solution, the assumption makes computations simple and is good enough to give an idea of what one can expect in actual operation. Also, these calculations are limited only to the initial reaction mixture (time = 0).

The mixture will boil when the equilibrium pressure exerted by the mixture equals the total system pressure. The vapor pressure data for each component is presented in Table A-2:

TABLE A-2. VAPOR PRESSURE IN mm Hg

Component	Temperature, °F					
	100	120	140	160	180	210
Water[1]	49.05	87.48	149.26	245	388.27	730.17
HCl[2]	0.000373	0.0014	0.0038	0.01	0.0247	0.132
CCl_4	203.55	320	488.16	723.81	1049.52	1754.2
EDC[3]	140.52	222.73	340	502.71	722.4	1187.33
EDB	24.87	41.31	66.44	103.5	156.86	279.39
SO_2[3]	4424.4	6124.78	8274.96	10940.12	14185.43	20280.83
Naptha[3]	832.87	1190	1655	2247	---	---

[1] From Steam tables.

[2] From Perry.

[3] From Lange

Thus, equilibrium pressure exerted by the mixture at 100°F is:

$$\text{Equilibrium pressure} = (49.05)_{\text{water}} + (203.55 \times 0.153 + 140.52 \times 0.37)_{\text{organic phase}}$$
$$+ 0.374 \times 24.87 + 4424.4 \times 0.019 + 0.085 \times 832.87)$$
$$= 296.14 \text{ mm Hg.}$$

Similarly, the equilibrium pressure of the mixture is calculated at other temperatures and is given in Table A-3. It can be seen from this table that the normal boiling point of the mixture is between 140 and 160°F (i.e., 60-70°C).

If vacuum pump is used to remove the ethylene formed in the reactor, then the reactor will be operating at sub-atmospheric pressures and the boiling point would be much lower than 70°C. If the reactor contents boil off, there will be a significant loss of organics in the vapor phase leading to the problem of toxic emissions. This is illustrated in the subsequent calculations.

Assume reactor pressure is 672 mm Hg, i.e., mixture boils at 140°F. The equilibrium composition (mole fraction) of the vapor would be:

Water	0.222	≡ 4	lbs
CCl_4	0.11	≡ 16.94	lbs
EDC	0.187	≡ 18.51	lbs
EDB	0.037	≡ 6.95	lbs
SO_2	0.234	≡ 15.0	lbs
Naptha	0.210	≡ 15.12	lbs

Thus, organic loss would be:

$$\frac{16.94 + 18.51 + 6.95 + 15.12}{4} = 14.38 \ \frac{\text{lbs of organics}}{\text{lb of steam}}$$

This is not desirable. Hence, it is felt that the reactor should be operated at atmospheric pressure with the gases being removed by flowing a

TABLE A-3. EQUILIBRIUM PRESSURE FOR INITIAL REACTION MIXTURE

Temperature, °F	Pressure (mm Hg)
100	296.14
120	451.5
140	672
160	978.6

carrier gas like nitrogen or a fan. As a result, the vacuum pump has been eliminated from the process flow sheet. Also, the zinc is assumed to be fed using a carrier gas, eliminating the need for a feeder. This also shows that the idea of removing reaction heat by boiling off water is not very attractive. Moreover, if one calculates the heat of vaporization for the mixture at its boiling point, it would be less than 200 Btu/lb of vapor. Thus, the extent of heat removal by boiling the mixture is also not very efficient.

Gas Processing:

Ethylene will be produced at a rate of about 0.092 lb-mole/min (approximately 37 ft^3/min). It is a good idea to pass the reactor gases through a condenser before being sent to a flare. It is assumed that a condenser of about 100 ft^2 area would be adequate for this duty.

Other equipment:

Filter feed pump	30 gal/min
Filter	5.0 ft^2
Filtrate pump	30 gal/min
Effluent storage tank	5000 gallons

Reactor outlet composition:

Unreacted organics:	982 lbs
Water	685 lbs
Unreacted Zn	270 lbs
$ZnBr_2$	2340 lbs
$ZnCl_2$	1400 lbs
	5677

Effluents:

Organic effluents/batch = 982 lbs

Aqueous effluents/batch = 4425 lbs

Solids/batch = 270 lbs

Chloropicrin Formulations

Although IT test work indicates high acid consumption to solve the problem of zinc coating, it has been assumed that this problem can be solved without consuming excessive acid (e.g., better agitation, etc.).

Assuming 300 gallons of this formulation are treated per batch,

Amount of pesticide treated = 3948 lbs/batch

Assuming only EDB reacts with the zinc, the amount of zinc reqiured is:

Zn required at 20 percent excess = 640 lbs/batch

Amount of $ZnBr_2$ formed = 8.13 x 225 = 1830 lbs/batch

Amount of water required to dissolve the $ZnBr_2$ would be:

Water required = 64 gallons/batch

at 30 percent excess

30 percent HCl required = 3.35 gallons/batch

Reactor effluents:

Untreated organics = 2420 lbs

Water = 534 lbs

$ZnBr_2$ = 1830 lbs/batch

Unreacted zinc = 106 lbs/batch

REAGENT REQUIREMENTS

For CS_2-free EDB formulation:

Zn = 1620/3948 x 1,505,794 = 617,879 lbs
Water = 82 x 1,505,794/3,948 = 31,275 gallons
30% HCl = 4.1 x 9.5 x 1,505,794/3,948 = 14,850 lbs

Chloropicrin formulation:

Zn = 640/3948 x 865,095 = 140,240 lbs
Water = 64 x 865,095/3,948 = 14,025 gallons
30% HCl required = 3.35 x 95 x 865,095/3,948 x 6980 lbs

Pure EDB from distillation of CS_2 formulation (approximately 43,700 lbs)

Zn = 43,700/187.87 x65.38 x 1.2 = 18,250
Water required = 1825 gallons
30% HCl required = 870 lbs

Total zinc = 776,370 lbs
Water = 47,125 lbs
30% HCl = 22,710 lbs

ATEG PROCESS

The ATEG process was described in detail in Section 3. Preliminary calculations to estimate reagent requirements and equipment sizes are presented in this section. The following primary assumptions were made:

1. Batch operation.

2. A total of 300 gallons of pesticide is treated per batch.

3. Chloropicrin formulations cannot be treated with this process.

4. Formulations containing CS_2 are distilled to recover approximately 100 percent pure EDB. Because the amount of pure EDB is small and treating pure EDB by ATEG may be dangerous (RTI, 1987), it is assumed that the pure EDB is mixed with a CS_2-free formulation at Liberty. The composition of the resulting formulation is shown in Table A-4.

5. The density of the pesticide formulation is 13.16 lb/gallon.

6. Both EDB and EDC undergo complete dehalogenation in the ATEG process.

7. Other constituents in the formulation do not undergo any reaction. Although in actual operation this is not going to be the case, it is a valid engineering assumption. The amount of other constituents is small and hence neglecting their contributions to raw material consumption and equipment sizing will not alter the overall cost estimates substantially.

TABLE A-4. COMPOSITION OF PESTICIDE FORMULATION ASSUMED FOR ATEG

Component	Weight, %
EDC	25.0
CCl_4	16.1
EDB	51.0
SO_2	0.2
Naphtha	4.3
MeCl	1.2
Other	2.2

The reaction proceeds in two steps:

STEP 1 (Reaction 1)

$$C_2H_4X_2 + AOH \xrightarrow[\text{catalyst}]{\text{TEG}} C_2H_3X + AX + H_2O$$

STEP 2 (Reaction 2)

$$C_2H_3X + AOH \xrightarrow[\text{catalyst}]{\text{TEG}} C_2H_2 + AX + H_2O$$

where

X = halogen, Cl or Br

A = Alkali, Na or K

Only the first reaction takes place in the reactor in the presence of sodium hydroxide. The vinyl halides (C_2H_3X) are eliminated in the scrubber by reacting with potassium hydroxide (KTEG).

Additional assumptions are stated whenever they are made in the course of the calculation.

Reactor

A total of 300 gallons of pesticide is treated per batch. At a density of 13.16 pounds per gallon, this equals 3948 lb/batch. Therefore, amounts of EDB and EDC treated per batch are as follows:

EDB = 0.509 x 3948 = 2009.5 lb or 10.7 lb-moles/batch

EDC = 0.25 x 3948 = 987.0 lb or 9.97 lb-moles/batch

EPA has proposed the use of solid NaOH flakes in the reactor. In earlier tests conducted by EPA and later by IT, twice the theoretical amount of NaOH was used in the reactor to convert EDB to vinyl bromide. However, discussions with IT suggested that using theoretical amount of NaOH (with some excess) should be able to carry out the first reaction (STEP 1). NaOH in 20 percent excess of the theoretical requirement would be fed to the reactor. Thus,

$$\text{NaOH fed} = (9.97 + 10.7) \times 40 \times 1.2$$

$$= 992 \text{ lb}$$

$$\text{NaOH feed rate} = \frac{992}{60} = 16.53 \text{ lb/min}$$

The pesticide feeding operation is assumed to be completed in 10 minutes. Thus, the pesticide feed rate is 30 gpm. The TEG is fed at 1 percent of total pesticide or 0.01 x 300 is 3 gallons. Assuming 1 hour as the feeding time, the TEG feed rate is 0.05 gpm or 3 gph.

The reaction products and their quantities are:

Reactor Liquid Effluents

Liquid effluents are as follows:

	lb/batch
Unreacted organics	929.8
Water	372.1
NaCl	583.2
NaBr	1101.0
Unreacted NaOH	165.3

The amount of water formed due to reaction is as follows:

$$20.67 \times 18 = 372 \text{ lb}$$

Solubility of NaCl in water = 1 lb/2.8 lb water

Solubility of NaBr in water = 1 lb/1.1 lb water

Solubility of NaOH in water = 1.3 lb/1 lb water

Assuming that the salts dissolve in the water up to their saturation units

$$\text{NaCl dissolved in water} = \frac{1}{2.8} \times 372 = 133 \text{ lb}$$

$$\text{NaBr dissolved in water} = \frac{1}{1.1} \times 372 = 338 \text{ lb}$$

$$\text{NaOH dissolved in water} = 1.3 \times 372 = 484 \text{ lb}$$

Undissolved solids

Undissolved solids are as follows:

NaCl = 450.2 lb

NaBr = 763.0 lb

Total undissolved solids = 1213.2 lb

% solids in slurry = 38.5 (too high)[1]

[1] The percentage solids in the reactor is very high and can create mixing, pumping, and heat transfer problems. The reaction mixture will have to be diluted by adding water to the reactor. Another way to do the same thing is to use NaOH solution, instead of solid NaOH. In fact using NaOH solution will eliminate problems of having to transport and feed solid NaOH. Also, the use of caustic solution will make heat removal from the reactor easier.

It is assumed that the solids are separated in a filter having 5 ft² of filtration area.

Reactor Effluent Processing Units:

Filter feed pump:	30 gpm
Filter:	5 ft²
Filtrate pump:	30 gpm
Storage pump:	4000 gallon capacity

Total effluent from the reactor = 3151.4 lbs.

Liquid effluent = 1938.2 lbs
Solid effluent = 1213.2

Heat Effects in Reactor

The heat of reaction can be calcuiated from the heat of formation data. For the reactions occuring in the reactor, the heats of reaction are:

$$(\Delta H_R)_{ED_B} = 25{,}610 \text{ Btu/lb-mole}$$

$$(\Delta H_R)_{EDC} = 31{,}970 \text{ Btu/lb-mole}$$

Thus, the overall heat liberated in Btu/hr is:

$$(\Delta H_R) = \frac{10.7}{1.5} \times 25{,}610 + \frac{9.97}{1.5} \times 31{,}970$$

$$= 395{,}170 \text{ Btu/hr}$$

The rate of heat removal from the reactor jacket can be calculated as:

$$Q = UA\,\Delta t_{ln}$$

Assuming U = 100 Btu/hr ft²°F

$$\Delta t_{ln} = 40°F$$

A (for 500 gallon reactor) $\simeq$ 80 ft²

(N.B. Water will have to be added to the reactor, minimum 500 lbs, to maintain percentage of solids below 20 percent.)

$$Q = 100 \times 80 \times 40$$

$$= 320{,}000 \text{ Btu/hr}$$

There, heat gained by the reaction system would be:

$$q = 395{,}170 - 320{,}000$$

$$= 75{,}170 \text{ Btu/hr}$$

Total heat gained over the reaction period would be:

$$q' = 75{,}170 \times 1.5$$

$$= 122{,}755 \text{ Btu}$$

The heat gained will raise the reactor temperature. Assuming average run in reactor is about 3948 lb, we have:

$$q' = m \times C_p \times \Delta t$$

$$\Delta t = 112{,}755/(3948 \times 0.8)$$

$$= 35.7°F$$

$$\Delta t = 20°C \text{ (acceptable)}$$

GAS PROCESSING

The gases from the reactor are treated in a scrubber by KTEG solution, which is a mixture of KOH and TEG in 1:1 molar ratio to remove vinyl halides from the gaseous effluents. The KTEG is diluted with water to give about 40 percent KTEG solution. The molecular weights of KOH and TEG are 56.09 and 194.23, respectively.

Thus, the mass of KTEG solution containing 1 lb-mole of KOH is:

$$\frac{(56.09 + 194.23)}{0.4} = 625.8 \text{ lb}$$

The density of the KTEG solution is reported to be 1.26 g/cm^3. Thus, the volume of KTEG solution that contains 1 lb-mole of KOH is:

$$V = \frac{625.8}{1.26 \times 62.43} \times 7.481 = 59.55 \text{ gal}$$

The KOH reacts with the vinyl halides from the reactor to produce acetylene and potassium salt (see Reaction 2). For every mole of vinyl halide, 1 mole of KOH is required. The reactor and the scrubber operate simultaneously. The scrubber operation time is the same as the reactor operation time, i.e., 1.5 h. Assuming, uniform gas loading, the vinyl halide feed rate to the scrubber is:

$$(9.97 + 10.7) \frac{1}{1.5 \times 60} = 0.23 \text{ lb-mole/min}$$

Therefore, the KOH feedrate to the scrubber = 0.23 lb-mole/min

At 20 percent excess, the KOH required = 0.28 lb-mole/min

Thus, volumetric feed rate of KTEG to scrubber is 16.7 gal/min.

Packed Tower Design

ρ_L = density of liquid = 78.7 lb/ft^3

ρ_g = density of gas = 0.204 lb/ft^3

L' = liquid flow in lb/min = 175.42 lb/min

G' = gas flow at 20% excess in lb/min = 23.64 lb/min

The EPA has proposed to use a packed-column scrubber with countercurrent gas-liquid flow. Flexipac packings, Type 2, will be used in this packed column. Referring to the flooding chart for these packings (Figure A-1), the x-coordinate is:

$$\frac{L}{G} \left(\frac{\rho_V}{\rho_L - \rho_V}\right)^{\frac{1}{2}} = 0.38$$

Thus, from the chart

$$\frac{G^2 \rho_F}{\rho_V \rho_L g_c} \text{ at flooding} = 0.06$$

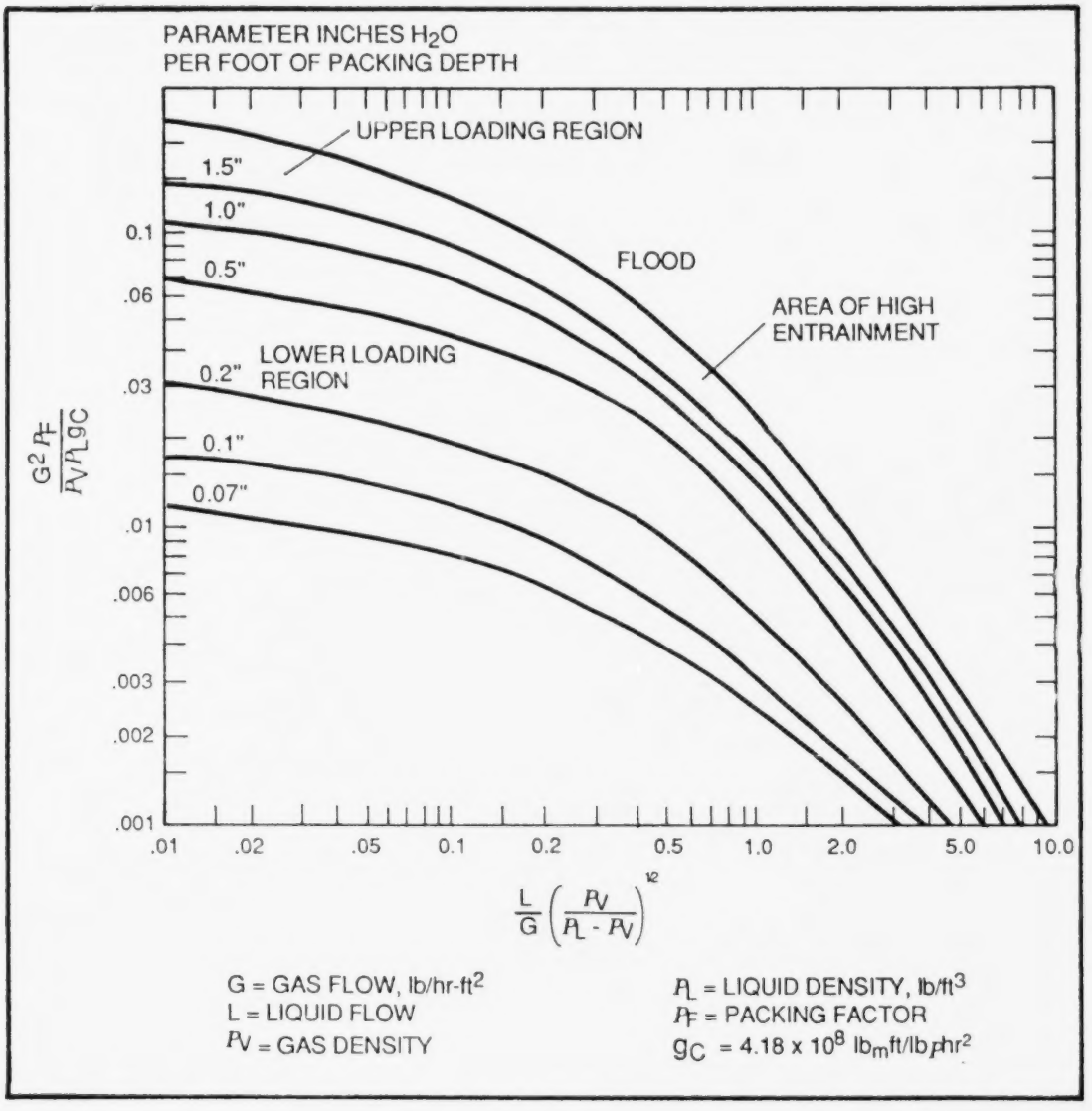

Figure A-1. Generalized pressure drop correlation for flexipac packings. (Koch Engineering Company, Inc.).

where G = lb/h per ft^2 of gas

ρ_F = packing factor = 22

Thus,

G = 71.13 lb/min ft^2 at flooding

The column is designed at 60 percent of flooding flow rate. Thus,

Design G = 0.6 x 71.13

= 42.7 lb/min ft^2

Thus, the cross-sectional area of the column = G'/G = 23.64/42.7 = 0.554 ft^2, and the diameter of the column would be 0.84 ft (1 ft was assumed for column diameter). EPA has calculated a scrubber height of about 20 ft. for this application.

Acetylene produced in the scrubber is removed by a vacuum pump and flared to produce CO_2 and H_2O. The volume that the vacuum pump needs to handle is calculated as 130 cfm, assuming ideal gas laws.

Reaction Products

Amount of KCl formed = 0.11 $\frac{\text{lb-mole}}{\text{min}}$ = 8.2 lb/min

Amount of KBr formed = 0.12 $\frac{\text{lb-mole}}{\text{min}}$ = 14.3 lb/min

Amount of water formed = 0.23 $\frac{\text{lb-mole}}{\text{min}}$ = 4.14 lb/min

Each salt is assumed to dissolve independently.

Amount of water required by KCl for complete disolution

= 18.5 lb/min

Amount of water required by KBr for complete disolution

= 17.06 lb/min

Amount of water available with KTEG = 105 lb/min.

Thus, sufficient water is available for the salts to dissolve completely.

The capacity of the KTEG holding tank is as follows:

Capacity = 16.7 gpm x 1.5 x 60 x 1.3 = 1954 gal (assume 2000-gallon capacity tank)

Heat Effects in Scrubber

The heat of reactions carried out in the scrubber are:

Vinyl chloride reaction (ΔH_R) = 13,860 Btu/lb-mole

Vinyl bromide reaction (ΔH_R) = 12,270 Btu/lb-mole

Thus, heat liberated per hour would be:

$$(\Delta H_R) = \frac{10.7}{1.5} \times 12{,}270 + \frac{9.97}{1.5} \times 13{,}860$$

$$= 179{,}650 \text{ Btu/hr}$$

This heat will raise the temperature of the liquid phase (where the reaction occurs) and part of it will be lost to the gas phase. Assuming that the entire heat of reaction is contained only in the liquid phase (worst case scenario), then the rise in temperature of the liquid phase in the scrubber is:

$$(\Delta H_R) = \text{Mass} \times \text{sp. ht.} \times \Delta t$$

$$179{,}650 = (175.42 \times 60) \times 0.8 \times \Delta t$$

Thus, $\Delta t = 21.34°F$

$= 12°C$ (not much, acceptable)

However, the scrubber effluent is mixed with the feed tank solution (2000 gallons) and thus, the overall temperature rise of the feed mixture

will be negligible. However, to tackle any unusual temperature effects during operations, a heat exchanger of 50 sq. ft. per scrubber is recommended.

Reagent Requirements for ATEG Process

From the earlier calculations, the reagent requirements in the reactor are:

NaOH = 992 lbs/batch

TEG = 3 gals/batch = $\frac{3}{7.481}$ x 62.43 x 1.25 = 31.25 lbs/batch

Scrubber Section

The KTEG solution is used in the scrubber to convert the vinyl halides to acetylene. Since this solution contains substantial amount of the TEG, it will not be economical to discard the spent solution at scrubber outlet. EPA has suggested that the spent solution be collected in the KTEG feed tank, and thus, reciruclate the TEG. KOH will have to be added to the feed tank to replenish the KOH that has reacted, and thus, maintain the concentration driving force for complete removal of vinyl halides in the reactor. With this mode of operation, the KTEG solution will soon become saturated with the potassium salts, and as a result, the scrubber effluent solution will contain suspended solids. To minimize the amount of solids in the scrubber, the scrubber feed solution will be filtered before being fed to the scrubber. It has been assumed that 2000 gallons of KTEG solution would be prepared, which can be used for about 100 batches (EPA's estimate) without the need for regeneration.

KOH requirement = (KOH reqd. for reaction)

+ (KOH for preparing feed solution)

TEG requirement = TEG required to prepare feed mixture.

The total amount that needs to be treated = 1,549,477 lbs.

Amount treated per batch = 3948 lbs.

No. of batches = 1,549,477/3948

= 393 batches

Thus for the Reactor:

NaOH required = 992 x 393 = 389,856

TEG = 31.25 x 393 = 12,281.25

For Scrubber:

$$KOH = 1420 \times 393 + 1860 \times \frac{393}{100}$$

(for reaction) (to prepare feed solution)

= 565,370 lbs

$$TEG = 6600 \times \frac{393}{100} = 25,940 \text{ lbs}$$

STARVED-AIR INCINERATION CALCULATIONS

In a conventional combustion process (excess-air incineration), the bromine in the waste is oxidized to Br_2. The Br_2/HBr thermodynamics favors Br_2 formation. The Br_2 can be reduced to HBr in presence of water vapor, and the reaction mechanism is represented as follows:

$$Br_2 + H_2O \rightleftharpoons 2\ HBr + \tfrac{1}{2}\ O_2$$

The equilibrium constant for this reaction is given by the following equation:

$$Kp = \frac{P_{HBr}^{2}\, P_{O_2}^{\frac{1}{2}}}{P_{Br_2}\, P_{H_2O}} \qquad \text{(Eq. 1)}$$

where the partial pressures of HBr, O_2, Br_2 and H_2O are under equilibrium conditions.

It is apparent from the preceding that if the partial pressure of oxygen is reduced close to zero, the partial pressure of HBr increases substantially (tending towards unfinity), which implies almost exclusive HBr formation. This is the principle used in the starved-air incineration concept. In starved-air incineration, however, the oxygen is not completely eliminated; instead, it is supplied at substoichiometric levels.

A rearrangement of Equation 1 gives the following:

$$\frac{P_{HBr}^{2}}{P_{Br_2}} = Kp\, \frac{PH_2O}{P_{O_2}^{\frac{1}{2}}} \qquad \text{(Eq. 2)}$$

Assuming $P_{H_2O}/P_{O_2}^{\frac{1}{2}} = 0.8$ (estimate provided by John Zink Co.) and an incineration temperature of 1800°F (Kp for HBr/Br_2 system at 1800°F is 5.9×10^{-3}), then:

$$\frac{P_{HBr}^{2}}{P_{Br_2}} = 5.9 \times 10^{-3} \times 0.8$$

$$= 0.00472$$

Assuming $P_{Br_2} = 0.0008$ (estimate provided by John Zink Co.)

$$P_{HBr} = 0.002$$

$$\frac{P_{Br_2}}{P_{HBr}} = 0.4$$

Therefore, for every 100 moles of HBr formed, 40 moles of Br_2 will be formed. Thus, the bromine formation may not be substantially reduced.

As indicated earlier, calculations at the scrubber temperature are more relevant. The typical flue gas temperature at the scrubber inlet is about 200°F; however, Kp data is available at a minimum temperature of 1000°F. The Kp at 1000°F is 3.2×10^{-6}.

Assuming $P_{H_2O}/P_{O_2}^{\frac{1}{2}} = 0.8$, we get

$$\frac{P_{HBr}^2}{P_{Br_2}} = 3.2 \times 10^{-6} \times 0.8$$

$$= 2.53 \times 10^{-6}$$

Assuming $P_{Br_2} = 0.0008$

$$P_{HBr} = 45 \times 10^{-6}$$

$$\frac{P_{Br_2}}{P_{HBr}} = 17.8$$

Thus, at 1000°F, almost exclusive Br_2 formation will occur (about 95%). At 200°F, even traces of HBr will be converted to Br_2 (i.e., the gas will consist of all bromine).

APPENDIX B

COST-ESTIMATING PROCEDURES AND RESULTS

INTRODUCTION

The costs reported in Section 4 for the chemical destruction processes are based on capital and annual cost estimates prepared by PEI. These estimates were developed in order to provide comparable cost numbers to the quotes received from the incineration facility operators. The costs are based on the preliminary process designs developed by PEI in conjunction with the EPA process developers. These designs are based on the process calculations and performance assumptions reported in Appendix A. In order to achieve higher processing rates, it is assumed that two trains of equipment will be in operation during a batch.

COST ESTIMATES

A summary of the cost estimates prepared for the ATEG and Zn process design variations is presented in Table B-1. Detailed cost backup information for each ATEG and Zn process option is provided in Tables B-2 to B-4. Each cost backup table presents a detailed capital and annual cost breakdown.

COST ESTIMATION PROCEDURE

The costs associated with building and operating a plant fall into two categories: capital investment and operation and maintenance (O&M) costs. Capital investment includes the cost of procuring and installing the necessary equipment, complete with piping, instrumentation, and services plus the capital required for the initial startup of the facility. The capital needed

TABLE B-1. COST ESTIMATE SUMMARY

ZN PROCESS - NEW FACILITY[a]		
Total Capital Investment		$1,015,000[b]
Annual O&M Charge		$1,198,100[b]
UNITIZED COST	Subcontracted to small scale chemical manf.	Government owns and operates the facility
$/gallon	3.91[c]	6.43[d]
$/lb	0.3[c]	0.49[d]
ZN PROCESS - OPTION OF USING GARD EQUIPMENT[a]		
Total Capital Investment		$ 532,800[b]
Annual O&M Charge		$1,130,000[b]
UNITIZED COST	Subcontracted to small scale chemical manf.	Government owns and operates the facility
$/gallon	Not applicable	5.82[d]
$/lb		0.44[d]
ATEG PROCESS - NEW FACILITY		
Total Capital Investment		$1,572,100[e]
Annual O & M Charge		$ 851,200[e]
UNITIZED COST	Subcontracted to small scale chemical manf.	Government owns and operates the facility
$/gallon	4.50[f]	10.32[d]
$/lb	0.34[f]	0.78[d]
ATEG - OPTION WITH GARD EQUIPMENT		
Total Capital Investment		$ 973,900[e]
Annual O & M Charge		$ 815,300[e]
UNITIZED COST		Government owns and operates the facility
$/gallon	Not applicable	9.39[d]
$/lb	Not applicable	0.71[d]

[a] Costs for zinc process have been evaluated assuming very minimal HCl consumption. If HCl consumption is high, the cost figures will be higher.

[b] Excludes costs for permitting and land lease. Assumes that steam, cooling water, and compressed air are available on site at no extra cost.

[c] A 10-year life span with straight line depreciation and zero salvage value.

[d] Carrying cost was taken to be the entire fixed capital cost.

[e] Excludes costs for permitting, disposal of chloropicrin stock and land lease. Assumes that steam, water, compressed air and other utilities are available on site at no extra cost.

[f] Assumes 10-year life span with straight line depreciation and zero salvage value. Also, the amount of pesticide treated excludes the amount of chloropicrin formulations.

TABLE B-2.

ATEG PROCESS
NEW DESIGN
April 87 $

PURCHASED EQUIPMENT COST

EQUIPMENT	SPECIFICATION	$/UNIT	QTY	$	
NaOH storage bin	SS304/FRP LINED; 18500 lb cap.	15,400	1	15,400	
NaOH feeder	SS316 construction	3,000	2	6,000	
Pesticide feed pump	Centrifugal, 30 gpm	1,700	2	3,400	
TEG feed pump to reactor	Metering pump, 3 gph cap.	1,100	2	2,200	
Reactor	500 gal cap, mixer 5hp motor	41,000	2	82,000	
Filter feed pump	Centrifugal, 30 gpm	1,700	2	3,400	
Filter	SS304, assume area of 5 sq.ft.	15,400	2	30,800	
Filtrate pump	Centrifugal, 30 gpm	1,700	2	3,400	
Storage/Phase separator	SS304, 4000 gal	40,200	1	40,200	
Scrubber	1'x20'ht., SS316	20,000	2	40,000	
Scrubber ht. trans. area	50 sq.ft. per scrubber	1,500	2	3,000	
Scrubber eff. vac.pump	130 cfm, 7.5 hp motor	6,800	2	13,600	
Flare & Stack		40,000	1	40,000	
KTEG storage tank	2000 gal, SS 304 const. with mixer	20,300	1	20,300	
Feed pump to scrubber	SS316 wetted parts, 17 gpm	1,000	2	2,000	
KOH storage bin	14000 lb cap.	11,400	1	11,400	
Makeup TEG feed pump		1,000	2	2,000	
KOH feeder	SS316 construction	3,000	2	6,000	
Reactor O/H condensor	100 sq. ft. of heat transfer area	4700	2	9,400	
Scrubber feed filter	SS304/FRP, assume 5 sq.ft. area	16,600	2	33,200	
	Purchased Equipment Cost			367,700	
CONSTRUCTION EXPENSE					
Installation				143,400	
Instrumentation & control				36,800	
Piping installed				91,900	
Electrical Installations				36,800	
Buildings				147,100	
Yard Improvement				36,800	
Service facilities				147,100	
	Total Construction Expense			639,900	
	TOTAL DIRECT CAPITAL COST (PEC + CONSTRUCTION EXP)				1,007,600
INDIRECT COST					
Engineering and supervision				110,300	
Construction				100,800	
Contractors fee				80,600	
	Indirect Cost			291,700	
	TOTAL DIRECT AND INDIRECT COST				1,299,300

(continued)

TABLE B-2. (Continued)

CONTINGENCY		129,900
FIXED CAPITAL		1,429,200
OTHER CAPITAL COSTS		
Working Capital	142,900	
Total Other Cost	142,900	
TOTAL CAPITAL COST		1,572,100

Note: 1) Pesticide formulations are assumed to be fed directly from tank cars
2) TEG will be fed directly from the TEG barrels.
3) It is assumed that land will be leased by EPA, and hence it is not not considered as a capital expense. Land lease will be an operating expense.
4) The cost of building may be eliminated if it is decided to have the plant in open with a small shed for housing controls.

(continued)

TABLE B-2. (Continued)

ANNUAL OPERATING & MAINTAINANCE COST

OPERATING COSTS				
Labor (@ $20/hr)			83,800	
Supervisory Labor			25,100	
Consumables				
RAW MATERIAL				
	$/lb	Qty. (lbs)	Total Cost	
NaOH	0.24	513000	123,100	
TEG	0.67	38250	25,600	
KOH	0.43	642500	276,300	
Total Raw Material Cost			425,000	
UTILITIES				
Electricity (@ 5 cents/kw-hr)			600	
			600	
Total Operating Cost				534,500
MAINTAINANCE				
Labor			45,700	
Material			68,600	
Total Maintainance Cost				114,300
Operating Supplies.				9,300
OVERHEADS				
Payroll Cost			46,400	
Plant Indirects				
Investment Portion			57,200	
Labor Portion			69,600	
Administrative Expense			30,900	
Miscellaneous			15,500	
Total Overhead Expense				219,600
OTHER OPERATIONAL EXPENSES				
Disposal of reactor effluents			226,900	
Disposal of scrubber effluents			41,100	
Cost of Distilling the Liberty Samples			140,900	
Credit for Products of Distillation			(435,400)	

(continued)

TABLE B-2. (Continued)

Total Other Operational Expense	(26,500)
TOTAL OPERATION AND MAINTAINANCE CHARGE	851,200

	Govt. owns and operates the facility	Subcontracted to small scale chemical mfr.
CARRYING CHARGE	1,429,200	142,900
UNITIZED COST		
$/GALLON (Approx 220,900 gallons)	$10.32	$4.50
$/LB (Approx 2,915,100 lbs)	$0.78	$0.34

Note: 1) Labor cost is computed assuming 3 operators and 1 lab technician per shift, 8 hrs/shift, 3 batches per shift, 393 batches. This assumes a very efficient operation.

2) Utilities costs have been calculated assuming steam, water and compressed air requirements are minimal; thus, contribution to cost is negligible.

3) Cost of Raw Materials have been taken from the Chemical Marketing Reporter

4) Only carbon disulfide containing formulations are distilled (i.e. 785,245 lbs of low EDB and 624,031 lbs of high EDB formulations. Total amount distilled equals 1,409,276 lbs.)

5) The cost for distillation is assumed to be 10 cents per pound. This cost figure has been suggested by EPA. Carbon tetrachloride selling price is taken as $0.36/lb, while that of carbon disulfide is taken as $420/ton. Total carbon tetrachloride recovered = 1092803 lbs; carbon disulfide = 220055 lbs.

6) The cost/gallon and cost/lb figures shown above are exclusive of the following costs: 1) permitting, 2) land lease and 3) disposal of chloropicrin stock

7) Carrying charge for government owned facility is calculated to be the entire capital cost, while that for subcontracting to a small scale chemical manufacturer, is calculated assuming 10 year life span, straight line depreciation and zero salvage value.

8) The approximate amount of pesticides treated excludes the amount of chloropicrin formulations.

9) NaOH used is commercial grade (76 %).

10) KOH used is commercial grade (88 %).

11) Disposal of reactor effluents - 50c/lb for organics; 50c/gallon for aqueous waste organics: 930 lbs/batch; aqueous waste: 2250 lbs/batch at 10 lbs/gal; 393 batches

12) Disposal of scrubber effluents - 50c/lbs for organics; 50c/gallon for aqueous waste and salts organics: 6600 lbs every 100 batches; aqueous waste: 14030 every 100 batches at 10 lbs/gal 2400 lbs of salt for 380 batches at 10 lbs/gal density.

TABLE B-3.

ATEG PROCESS
OPTION OF UTILIZING GARD EQUIPMENT
April 87 $

PURCHASED EQUIPMENT COST

EQUIPMENT	SPECIFICATION	$/UNIT	QTY	$
NaOH storage bin	SS304/FRP lined; 18500 lb cap.	15,400	1	15,400
NaOH screw conveyor	SS316 construction	3,000	2	6,000
Pesticide feed pump	Centrifugal, 30 gpm	1,700	2	3,400
TEG feed pump to reactor	Metering pump, 3 gph cap.	1,100	2	2,200
Reactor	500 gal cap, mixer 5 hp motor	0	2	0
Filter feed pump	Centrifugal, 30 gpm	1,700	2	3,400
Filter	SS304, assume 5 sq.ft.	0	2	0
Filtrate pump	Centrifugal, 30 gpm	1,700	2	3,400
Storage/Phase separator	SS304, 4000 gal	40,200	1	40,200
Scrubber	1'x20'ht., SS316	20,000	2	40,000
Scrubber ht. trans. area	50 sq.ft. per scrubber	1,500	2	3,000
Scrubber eff. vac.pump	130 cfm, 7.5 hp motor	6,800	2	13,600
Flare and Stack		0	1	0
KTEG storage tank	2000 gal, SS 304 const.	20,300	1	20,300
Feed pump to scrubber	SS316 wetted parts, 17 gpm	1,000	2	2,000
KOH storage bin	14000 lb cap.	11,400	1	11,400
Makeup TEG feed pump		1,000	2	2,000
KOH screw feeder		3,000	2	6,000
Reactor O/H condensor	100 sq. ft. heat transfer area	4,700	2	9,400
Scrubber feed filter	SS304/FRP, assume 5 sq.ft. area	16,600	2	33,200
	Purchased Equipment Cost			214,900

CONSTRUCTION EXPENSE

Installation	
Instrumentation & control	143,400
Piping installed	36,800
Electrical Installations	91,900
Buildings	36,800
Yard Improvement	147,100
Service facilities	36,800
	147,100
Total Construction Expense	639,900
TOTAL DIRECT CAPITAL COST (PEC + CONSTRUCTION EXP)	854,800

(continued)

TABLE B-3. (Continued)

INDIRECT COST		
Engineering and supervision	110,300	
Construction	85,500	
Contractors fee	68,400	
Indirect Cost	264,200	
TOTAL DIRECT AND INDIRECT COST		1,119,000
CONTINGENCY		111,900
FIXED CAPITAL		1,230,900
OTHER CAPITAL COSTS		
Working Capital	142,900	
Total Other Cost	142,900	
TOTAL CAPITAL COST		1,373,800

Note: 1) Pesticide will be fed from the tank cars.
2) TEG will be fed from TEG barrels.
3) GARD facility reportedly has reactors, belt filter press, flare and stack which could be used for the present application.
4) Land will be leased by EPA. The leasing cost will come under operating expenses.
5) Cost of building may be eliminated if low cost shed or trailer is is used to house controls etc.

(continued)

TABLE B-3. (Continued)

ANNUAL OPERATING & MAINTAINANCE COST

OPERATING COSTS				
Labor (@ $20/hr)			83,800	
Supervisory Labor			25,100	
Consumables				
RAW MATERIAL				
	$/lb	Qty. (lbs)	Total Cost	
NaOH	0.24	513000	123,100	
TEG	0.67	38250	25,600	
KOH	0.43	642500	276,300	
Total Raw Material Cost			425,000	
UTILITIES				
Electricity (@ 5 cents/kw-hr)			600	
			600	
Total Operating Cost				534,500
MAINTAINANCE				
Labor			44,300	
Material			66,500	
Total Maintainance Cost				110,800
Operating Supplies				9,200
OVERHEADS				
Payroll Cost			46,000	
Plant Indirects				
Investment Portion			55,400	
Labor Portion			68,900	
Administrative Expense			30,600	
Miscellaneous			15,300	
Total Overhead Expense				216,200
OTHER OPERATIONAL EXPENSES				
Disposal of reactor effluents			226,900	
Disposal of scrubber effluents			41,100	
Cost of Distilling the Liberty Samples			140,900	
Credit for Products of Distillation			(435,400)	

(continued)

TABLE B-3. (continued)

Total Other Operational Expense	(26,500)
TOTAL OPERATION AND MAINTAINANCE CHARGE	844,200

	Govt. owns and operates the facility.	Subcontracted to small scale chemical mfr.
CARRYING CHARGE	1,230,900	NA
UNITIZED CHARGE		
$/GALLON (Approx. 220,900 gallons)	$9.39	
$/LB (Approx 2,915,100 lbs)	$0.71	

Note: 1) The labor cost is calculated assuming 3 operators and 1 lab technician, 8 hrs/shift, 3 batches/shift, 393 batches, $20/hr.
2) Utilities costs have been calculated assuming steam, cooling water and compressed air requirements are minimal; thus, contribution to cost is negligible.
3) Cost of raw materials have been taken from the Chemical Marketing Reporter.
4) Only carbon disulfide containing formulations are distilled (i.e. 785,245 lbs of low EDB and 624,031 lbs of high EDB formulations. Total amount distilled equals 1,409,276 lbs.)
5) The cost of distillation is assumed to be 10 cents per pound. This cost figure has been suggested by EPA. Carbon tetrachloride selling price is taken as $0.36/lb, while that of carbon disulfide is taken as $420/ton. Total carbon tetrachloride recovered = 1092803 lbs; carbon disulfide = 220055 lbs.
6) The cost/gallon and cost/pound figures shown above are exclusive of following costs: 1) permitting, 2) disposal of chloropicrin stock and 3) land lease expense.
7) Carrying charge for government owned facility is calculated to be the entire capital cost, while that for subcontracting to a small scale chemical manufacturer, is calculated assuming 10 year life span, straight line depreciation and zero salvage value.
8) The approximate amount of pesticide treated excludes the amount of chloropicrin formulations.
9) NaOH used is commercial grade (76 %).
10) KOH used is commercial grade (88 %).
11) Disposal of reactor effluents - 50c/lb for organics; 50c/gallon aqueous soln. 930 lbs/batch of organics; 2250 lbs of aqueous waste/batch, 10 lbs/gal. density
12) Disposal of scrubber effluents - 50c/lb for organics; 50c/gallon acqueous waste and salts. 6600 lbs of organics every 100 batches; 14430 lbs of aqueous waste every 100 batches at 10 lbs/gal density; 2400 lbs of salts for 380 batches at 18 lbs/gal density

TABLE B-4.

ZN PROCESS
NEW DESIGN
APRIL 87 $

PURCHASED EQUIPMENT COST

EQUIPMENT	SPECIFICATION	$/UNIT	QTY	$
Zn storage bin	SS304; 15000 lb cap.	6,800	1	6,800
Zn screw conveyor	SS construction	3000	2	6,000
Pesticide feed pump	Centrifugal, 30 gpm	1,700	2	3,400
HCl feed pump	Metering pump R/L, 1.5 gph cap.	1,200	2	2,400
Water feed pump	5 gpm cap, centrifugal	1,500	2	3,000
Reactor	500 gal cap, turbine impeller, 5hp	41,000	2	82,000
Filter feed pump	Centrifugal, 30 gpm	1,700	2	3,400
Filter	SS304, assume area of 5 sq.ft.	15,400	2	30,800
Filtrate pump	Centrifugal, 30 gpm	1,700	2	3,400
Storage/Phase separator	SS304, 4000 gal	40,200	1	40,200
External heat exchanger	SS304 const; 200 sq.ft.	8,000	2	16,000
Flare & Stack		40,000	1	40,000
Reactor O/H condenser	100 sq.ft. heat transfer area	4,700	2	9,400
	Purchased Equipment Cost			246,800

CONSTRUCTION COST

Installation	96,300	
Instrumentation & control	24,700	
Piping installed	61,700	
Electrical Installations	24,700	
Buildings	98,700	
Yard Improvement	24,700	
Service facilities	98,700	
Total Construction Expense	429,500	
TOTAL DIRECT CAPITAL COST (PEC + CONSTRUCTION EXP)		676,300

INDIRECT COST

Engineering and supervision	74,000	
Construction	67,600	
Contractors Fee	54,100	
Indirect Cost	195,700	
TOTAL DIRECT AND INDIRECT COST		872,000

(continued)

TABLE B-4. (Continued)

CONTINGENCY		87,200
FIXED CAPITAL		959,200
OTHER CAPITAL COST		
Working Capital	95,900	
Total Other Cost	95,900	
TOTAL CAPITAL COST		1,055,100

Note: 1. Pesticides will be fed from tank cars.
2. HCl will be fed from HCl barrels.
3. Land will be leased by EPA. The leasing cost will come under operating expenses.
4. Cost of building may be eliminated if low cost shed or trailer is used to house controls etc.

(continued)

TABLE B-4. (Continued)

ANNUAL OPERATING & MAINTAINANCE COST

OPERATING COSTS					
Labor (@ $20/hr)				150,200	
Supervisory Labor				45,100	
Consumables					
RAW MATERIALS					
	$/LB		QTY (LBS)	Cost ($)	
Zinc	0.47		776370	364,900	
HCl	0.03		22710	700	
	$/1000 GALLON				
Water	0.6		47200 GALLONS	0	
Total Raw Material Cost				365,600	
UTILITIES					
Electricity				2,100	
				2,100	
Total Operating Cost					563,000
MAINTAINANCE					
Labor				30,700	
Material				46,000	
Total Maintainance Cost					76,700
Operating Supplies					13,600
OVERHEADS					
Payroll Cost				67,800	
Plant Indirect Expense					
Investment Portion				38,400	
Labor Portion				101,700	
Administration Expense				45,200	
Miscellaneous Expense				22,600	
Distillation of CS2 formulation				140,900	
Credit for products of distillation				(435,400)	
Total Overhead Expense					(18,800)
DISPOSAL OF REACTOR EFFLUENTS					569,300

(continued)

TABLE B-4. (Continued)

TOTAL OPERATION AND MAINTAINANCE		1,203,800
	Govt. owns and operates the facility.	Subcontracted to small scale chemical mfr.
CARRYING CHARGE	959,200	95,900
UNITIZED COST		
$/GALLON (Approx 330,000 gallons)	$6.55	$3.94
$/LB	$0.50	$0.30

Note:
1. The above cost figures are calculated assuming that HCl consumption is minimal
2. The $/gal and $/lb figures shown above are exclusive of permitting, transportation and land lease.
3. Carrying cost for government owned facility is calculated to be the entire capital cost, while that for subcontracting to a small scale chemical manufacturer is calculated assuming 10 years life span, straight line depreciation and zero salvage value.
4. Labor cost has been evaluated assuming 2 operators and 1 lab technician, 8 hrs/shift, 2 batches/shift, 626 batches and $20/hr.
5. The raw material costs have been taken from Chemical Marketing Reporter.
6. Utilities costs have been calculated assuming that steam, cooling water and compressed air requirements are minimal; thus, contribution to the cost is negligible.
7. The amount of pesticide treated is the total amount of all formulations that need to be treated.
8. Distillation costs are for the CS2 containing formulations. The cost is estimated similar to those estimated in the ATEG process.
9. Reactor effluent disposal cost: 50c/lb for organics; 50c/gal for aqueous waste
   Miscellaneous formulations: 982 lbs of organics/batch; 4695 lbs of aqueous soln/batch
   Chloropicrin formulation: 2420 lbs of organics/batch; 2470 aqueous sol/batch

(continued)

TABLE B-4. (Continued)

ZN PROCESS
OPTION OF USING GARD EQUIPMENT
APRIL 87 $

PURCHASED EQUIPMENT COST

EQUIPMENT	SPECIFICATION	$/UNIT	QTY	$
Zn storage bin	SS304; 15000 lb cap.	6,800	1	6,800
Zn screw conveyor	SS construction	3000	2	6,000
Pesticide feed pump	Centrifugal, 30 gpm	1,700	2	3,400
HCl feed pump	Metering pump R/L, 1.5 gph cap.	1,200	2	2,400
Water feed pump	5 gpm cap, centrifugal	1,500	2	3,000
Reactor	500 gal cap, turbine impeller, 5hp	0	2	0
Filter feed pump	Centrifugal, 30 gpm	1,700	2	3,400
Filter	SS304, assume area of 5 sq.ft.	0	2	0
Filtrate pump	Centrifugal, 30 gpm	1,700	2	3,400
Storage/Phase separator	SS304, 4000 gal	40,200	1	40,200
External heat exchanger	SS304 consti 200 sq.ft.	8,000	2	16,000
Flare & Stack		0	1	0
Reactor O/H condenser	100 sq.ft. heat transfer area	4,700	2	9,400
	Purchased Equipment Cost			94,000

CONSTRUCTION COST

Installation		96,300	
Instrumentation & control		24,700	
Piping installed		61,700	
Electrical Installations		24,700	
Buildings		98,700	
Yard Improvement		24,700	
Service facilities		98,700	
	Total Construction Expense	429,500	
	TOTAL DIRECT CAPITAL COST (PEC + CONSTRUCTION EXP)		523,500

INDIRECT COST

Engineering and supervision	28,200	
Construction	52,400	
Contractors Fee	41,900	
Indirect Cost	122,500	
TOTAL DIRECT AND INDIRECT COST		646,000

(continued)

TABLE B-4. (Continued)

CONTINGENCY		64,600
FIXED CAPITAL		710,600
OTHER CAPITAL COST		
Working Capital	71,100	
Total Other Cost	71,100	
TOTAL CAPITAL COST		781,700

Note: 1. Pesticides will be fed from tank cars.
2. HCl will be fed from HCl barrels.
3. Land will be leased by EPA. The leasing cost will come under operating expenses.
4. Cost of building may be eliminated if low cost shed or trailer is used to house controls etc.
5. The GARD facility reportedly has reactors, belt filter press, flare and stack which could be used for the present application.

(continued)

TABLE B-4. (Continued)

ANNUAL OPERATING & MAINTAINANCE COST

OPERATING COSTS				
Labor (@ $20/hr)			150,200	
Supervisory Labor			45,100	
Consumables				
RAW MATERIALS				
	$/LB	QTY (LBS)	Cost ($)	
Zinc	0.47	776370	364,900	
HCl	0.03	22710	700	
	$/1000 GALLON			
Water	0.6	47200 GALLONS	0	
Total Raw Material Cost			365,600	
UTILITIES				
Electricity			2,100	
			2,100	
Total Operating Cost				563,000
MAINTAINANCE				
Labor			30,700	
Material			46,000	
Total Maintainance Cost				76,700
Operating Supplies				13,600
OVERHEADS				
Payroll Cost			67,800	
Plant Indirect Expense				
Investment Portion			28,400	
Labor Portion			101,700	
Administration Expense			45,200	
Miscellaneous Expense			22,600	
Distillation of CS2 formulation			140,900	
Credit for products of distillation			(435,400)	
Total Overhead Expense				(28,800)
DISPOSAL OF REACTOR EFFLUENTS				569,300

(continued)

TABLE B-4. (Continued)

TOTAL OPERATION AND MAINTAINANCE		1,193,800
	Govt. owns and operates the facility.	Subcontracted to small scale chemical mfr.
CARRYING CHARGE	710,600	NOT APPLICABLE
UNITIZED COST		
$/GALLON (Approx 330,000 gallons)	$5.77	
$/LB	$0.44	

Note:
1. The above cost figures are calculated assuming that HCl consumption is minimal
2. The $/gal and $/lb figures shown above are exclusive of permitting, transportation and land lease.
3. Carrying cost for government owned facility is calculated to be the entire capital cost, while that for subcontracting to a small scale chemical manufacturer is calculated assuming 10 years life span, straight line depreciation and zero salvage value.
4. Labor cost has been evaluated assuming 2 operators and 1 lab technician, 8 hrs/shift, 2 batches/shift, 626 batches and $20/hr.
5. The raw material costs have been taken from Chemical Marketing Reporter.
6. Utilities costs have been calculated assuming that steam, cooling water and compressed air requirements are minimal; thus, contribution to the cost is negligible.
7. The amount of pesticide treated is the total amount of all formulations that need to be treated.
8. Distillation costs are for the CS2 containing formulations. The cost is estimated similar to those estimated in the ATEG process.
9. Reactor effluent disposal cost: 50c/lb for organics; 50c/gal for aqueous waste
   Miscellaneous formulations: 982 lbs of organics/batch; 4695 lbs of aqueous soln/batch
   Chloropicrin formulation: 2420 lbs of organics/batch; 2470 aqueous sol/batch

to provide the necessary manufacturing and plant facilities is called the "fixed-capital investment," whereas the capital required for the operation of the plant is called "working capital." The costs for the day-to-day operation of the plant are referred to as "operation and maintenance costs."

Cost estimates can be classified into five main categories:

- Order-of-Magnitude (Ratio Estimate; ± 50 percent).
- Study (Factored Estimate; ± 30 percent).
- Preliminary (Budget Authorization Estimate; ± 20 percent).
- Definitive (Project Control Estimate; ± 10 percent).
- Detailed (Firm Estimate based on complete engineering drawings, specifications, and site surveys; ± 5 percent).

As part of this project, a study estimate based on known major items of equipment was prepared for the ATEG and Zinc processes. Preliminary sizing calculations were performed for each of these processes (Appendix A) to arrive at approximate equipment sizes. The following two subsections contain an overview of the overall cost estimation procedure used.

FIXED CAPITAL INVESTMENT

The literature contains several methods for arriving at an approximate estimate of fixed capital and total capital costs. A procedure recommended by Peters and Timmerhaus (1983) was adopted for these estimates. This procedure involves estimating the cost of purchased equipment and then developing all other cost items as a percentage of the purchase equipment costs.

Purchased Equipment Cost

The costs of major purchased equipment items shown on the process flowsheet were estimated from vendor quotes and cost data available in Peters and Timmerhaus (1983) and The Richardson Rapid Systems Volume IV (1984). The costs were updated to 1987 dollars by use of the CEP cost indices.

Expenses

The following cost items are included under expenses. These expense items have been estimated as a percentage of the purchased equipment cost. For the option of utilizing the GARD equipment, however, these items have been calculated using the purchase equipment costs under the option of new design.

Purchased-Equipment Installation--

Equipment installation costs include labor, foundations, supports, platforms, construction expenses, etc. These costs normally vary from 25 to 55 percent of the purchased-equipment costs. For these estimates, they are assumed to be 39 percent of the purchased-equipment cost.

Instrumentation and Controls--

Depending on its complexity, the total cost of instrumentation, including the cost of the instruments, auxiliary equipment and materials, and installation labor, ranges from 6 to 30 percent of the purchased-equipment cost. For these estimates, this cost is assumed to be 10 percent of the purchased-equipment cost.

Piping--

The cost for piping includes the pipe itself, labor, valves, fittings, supports, and other accessories involved in the erection of all piping used directly in the process. Depending on the type of plant, piping costs can vary substantially. For a fluid/solid processing plant (such as those proposed), piping usually runs about 31 percent of the purchased-equipment cost. For purposes of these estimates, piping cost is assumed to be 25 percent of the total purchased-equipment cost.

Electrical Installations--

The cost of electrical installations consists primarily of installation labor and materials for power and lighting (building and service lighting is usually included under the heading of building and services costs). In most chemical plants, these costs amount to about 10 to 15 percent of the purchased equipment cost.

Buildings and Services--

The cost of buildings and services includes the expenses for labor, materials, and supplies involved in the erection of all buildings connected with the plant. Costs of plumbing, heating, lighting, ventilation, and similar building services are included. For a solid/fluid processing plant, such costs for a grass-roots new plant run about 47 percent of the total purchased-equipment cost. In these estimates, however, this cost component is assumed to be 40 percent of the purchased-equipment cost.

Yard Improvements--

This item includes the cost for fencing, grading, roads, sidewalks, railroad sidings, landscaping, and similar items. For a chemical plant, this cost varies from 10 to 20 percent of the purchased-equipment cost. For purposes of these estimates, the cost is assumed to be 10 percent of the purchased-equipment cost.

Service Facilities--

Utilities for supplying steam, water, power, compressed air, and fuel are part of the service facilities of an industrial plant. In chemical

plants, the cost for such facilities generally vary from 30 to 80 percent, and 55 percent is the average for a normal solid/fluid processing plant. Because of the small scale of these operations, however, this cost is assumed to be 40 percent of the purchased-equipment cost.

For the option of utilizing equipment at the GARD facility, the above costs were evalauted as a percentage of the purchased equipment cost for new design.

Indirect Costs

The succeeding subsections cover the costs included under Indirect Costs.

Engineering and Supervision--

These capital costs include design and engineering, drafting, purchasing, accounting, construction and cost engineering, travel, reproduction work, communications, and home office expense, including overhead. This cost is usually 30 percent of the purchased equipment cost.

Construction Expense--

This item includes temporary construction and operation, construction tools and rentals, home office personnel located at the construction site, construction payroll, travel and living expenses, taxes, insurance, and other construction overheads. This item is estimated to be 10 percent of the total direct costs.

Contractor's Fee--

This expense varies from 2 to 8 percent of the total direct costs. For these estimates, the contractor's fee is assumed to be 8 percent of the total direct costs.

Contingency

Contingency is usually included in capital investment estimates to compensate for unpredictable events, such as storms, floods, strikes, price changes, small design changes, errors in estimation, etc. Contingency factors commonly range from 5 to 15 percent of the total direct and indirect costs. A contingency factor of 10 percent has been used in these estimates.

OTHER CAPITAL COSTS

Included under this category are land and working capital.

Land

Typically, land cost is estimated at 5 to 8 percent of the purchased equipment cost. Because land is proposed to be leased land for this project, land is not included as a capital expense item. Instead, the lease cost would be considered in the O&M expenses.

Working Capital

Once the plant is installed and ready for startup, some changes are usually required to make it operational. The capital required to start up the plant is the part of the capital appropriated because it is essential for the successful completion of the venture. Typically, this expense runs about 8 to 10 percent of the total fixed capital investment.

OPERATION AND MAINTENANCE COSTS

These costs represent all costs associated with the operation of the plant. In these estimates, the following costs have been considered.

Direct Operating Labor

This item represents the labor directly responsible for the operation of the process (primarily operators). Cost is determined by computing the labor hours required to operate the plant and multiplying this value by the hourly rate.

Supervisory Labor

This item usually figured at 20 to 30 percent of the direct operating labor. The upper limits usually represent batch or complex processing. In these estimates, supervisory labor is assumed to be 30 percent of the cost of operating labor.

Consumables

Consumables refer to the cost of raw materials and utilities used in the process. The cost of raw materials is based on requirements estimated from the material balance calculations. The utilities include electricity, water, steam, and compressed air. Estimates of total utility consumption are based on the material and energy balance calculations.

Maintenance

For preliminary estimating purposes, the cost of maintenance varies from 6 to 10 percent (average of 8 percent) of the fixed capital investment and includes the cost of labor and material. The labor portion usually accounts for about 40 percent of the total maintenance cost.

Operating Supplies

Operating supplies include filter cloths, brooms, mops, instrument charts, etc., exclusive of those items listed on the manufacturing cost sheet. For estimation purposes, this cost is assumed to be 6 percent of the operating labor.

Overheads

Overheads represent operating costs not directly associated with the manufacturing activity, but they are none the less essential for carrying out the manufacturing activity.

Payroll Cost--

This item includes Workmen's Compensation, pensions, group insurance, paid vacations and holidays, Social Security, unemployment taxes, profit sharing, and fringe benefits. This cost is usually estimated at 25 to 50 percent of the cost of labor (including direct, supervisory, and maintenance). In these estimates, payroll cost is calculated at 30 percent of the total labor cost.

Plant Indirects--

These costs include items such as local taxes, insurance, and local plant service expenses (i.e., associated with railroad spurs, plant roads, fire protection, cafeteria, employee safety, parking lots, etc.) These costs are made up of two components: 1) investment factor and 2) labor factor. Estimation of both factors has been discussed in Uhl, 1978. For purposes of these estimates, the investment factor is assumed to be 4 percent of the fixed capital investment and the labor factor is a percentage of the total operating labor cost.

Administrative Expense--

Administrative expense includes expenses connected with the administrative activities of top management. Although not directly involved in manufacturing, these activities are essential for the smooth operation and coordination of all other activities, and are therefore included in the cost

analysis. This category includes the salaries of administrators, secretaries, accountants, typists, etc., as well as the cost of office supplies and equipment, outside communications, administrative buildings, etc. This expense item is usually estimated to be 20 to 30 percent of the total operating labor cost.

Miscellaneous--

This cost item, which includes such things as the cost of providing and maintaining special clothing required by the operators, is estimated as a percentage of the total operating labor cost.

Other Operational Expenses

Other costs that must be considered specifically for these estimates include permitting costs, transportation costs, and the cost of disposing of the reaction products. For the ATEG process, the cost of distilling the formulations containing carbon disulfide and the cost of disposing of the chloropicrin formulations also must be included to arrive at reasonable cost figures. The sum of all these costs would represent the annual operation and maintenance (O&M) costs. To find the total cost of disposing of the pesticide formulations, one must add the cost of using the equipment to the annual O&M cost. The typical life span of chemical equipment is about 11 years (Peters and Timmerhaus 1983). If the equipment is used throughout its life span, the cost due to the fixed capital would represent the depreciation charge.

Carrying Charge

This item represents the fixed capital depreciation charge for the option of subcontracting to a small scale chemical firm. The EPA has found one chemical facility that is interested in undertaking the destruction of

pesticide formulations. If this facility is used, the fixed capital charge would be that due to depreciation. The same is also true, if the EPA decides to build a new facility, provided they can later sell the equipment to a chemical firm or perhaps use the facility for other similar projects. In this case, the carrying charge has been estimated on the basis of an assumed 10-year life span., straight-line depreciation, and zero salvage value.

For the option of government owned and operated facility, the carrying charge has been taken to be the total fixed capital cost. Under this option it is assumed that the facility is built and used only for destroying the EDB formulations.

The sum of the O&M costs and the carrying charge provides the annual cost to own and operate the chemical pesticide destruction plant. These costs are unitized in terms of $/gallon and $/lb as a measure of cost-effectiveness.

APPENDIX C

INFORMATION OBTAINED FROM COMMERCIAL INCINERATION FACILITIES

The highlights of the discussions with the various commercial incineration facilities are presented here.

VESTA

- Transportable unit.
- Past Experience: Successful testing with pesticides and PCB's.
- Requires demoisturized feed.
- Doesn't have a permit at the moment. Could be a while before they get one.
- Two-stage scrubbing system. (High-energy venturi followed by packed scrubber).
- No past experience with brominated waste. Currently scrubbers are not refractory-lined and could become corroded. Refractory lining could combat corrosion.
- Interested in the project, but believe the technology will be difficult to develop and expensive.

SHIRCO

- Transportable unit.
- Infrared technology.
- Does not have permit at the moment.
- Permit applications for PCB testing are pending.
- Pilot plant available for bench-scale test burns. Permit application (RD&D - Administration) pending.
- This process can handle only solid waste or sludges. Thus, EDB will have to be mixed with a carrier substance before it could be destroyed.
- Bench-scale testing (Thermal Gravimetric Analyzer - TGA) will cost approximately $50,000. This test does not analyze the flue gas emissions.
- Process is equipped with low-energy venturi scrubber.

ENSCO

- Main unit in El Dorado.
- No full-scale experience with brominated waste.
- Did burn some brominated waste. Scrubber could not remove bromine from the flue gases. An orange gas was observed at the stack. Since then, ENSCO is very apprehensive about brominated waste and would not burn it unless a substantial amount of waste is involved. Indicated willingness to do the job in a transportable unit that processes 50 gal/min only if the operation could last more than a month.
- Reported refractory corrosion problem.

Rollins Environmental

- Do handle pesticides on a regular basis.
- Facilities in New Jersey, Louisiana, and Texas.
- Has past experience with brominated waste. Burned brominated waste at New Jersey facility. Did have problems of bromine emissions; however, they claim that this problem was taken care of by changing furnace operating conditions (proprietary).
- Suggested that the equipment has been designed to withstand any corrosion due to halogens.
- Costs for incineration vary from application to application. Average cost is about 50 to 75 cents per pound.
- Permits available.

John Zink

- They have presented a proposal to EPA for this project.
- Earlier test resulted in bromine emissions; however, they believe the problem could be solved.
- Further information available from EPA.

Chemical Waste Management

- Rotary kiln facility in Chicago, which is largest in the United States.
- Fixed-hearth incinerators at St. Louis.
- Chicago facility is equipped with wet scrubber system, whereas St. Louis facility has one furnace with wet scrubbing and one with dry scrubbing system (bag filters).
- Average costs for liquids is 25 to 45 cents/pound.
- Small quantities of brominated waste (0.5 lb/min) will have to be treated. At this rate, the packed scrubbers should be able to remove bromine with an alkali.
- Permits available (generic permit).

International Technology Corporation (IT)

Presented a detailed seminar to EPA on their capabilities, the options they would like to try, and past experience. Suggested that the new transportable HTTS system could handle the pesticide destruction. IT could not provide cost information that would be meaningful to the destruction of only the EDB stocks. IT reported that cost information for EDB destruction via the HTTS would be cost-effective only as part of a larger scope project that would involve EDB, Silvex, and Dinoseb.